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method of using the instrument has been described already by R. T. Elworthy (*Bulletin No. 31, Mines Branch, Dept. of Mines, Canada, 1920*), and a second, which has been found very useful, has been worked out for the present investigation by Mr. John Patterson, M.A. It is shown in Fig. 3.

The density balance consisted of a quartz bulb, *A*, 1.25 cm. in diameter, and an arm, *C*, about 10 cm. long, mounted on a rocking arm, *B*. The two points of this arm rested on jewels, and the arm had a protecting case around it, as shown by the dotted lines, so as to prevent the balance from getting out of the jewels. The end of the arm, *C*, was turned at right angles and moved along a scale, which could be easily read to 0.1 mm. In most forms of this instrument, the pressure in the density chamber is adjusted by either exhausting or admitting the gas very slowly until the correct pressure is obtained. This is usually a very troublesome operation, and to overcome it, a reservoir, *G*, was attached to the chamber, which permitted the pressure to be altered by simply raising or lowering the mercury reservoir. The reservoir was provided with a manometer, *H*, with a scale, the zero of which could be set on the lower limb of the manometer and the pressure read directly to 0.1 mm. The manometer, *H*, could be used either for pressures less than atmospheric, in which case the tube, *H*, was free of air, or for pressures greater than an atmosphere, when the seal at the top is taken out. The balance could be calibrated for a standard gas, such as air, by plotting pressures against the scale reading. Then, to obtain the density of a gas, all that was necessary was to wash out the density chamber thoroughly and take two or three readings at different parts of the scale. From these, the relative density could be determined at once. It was not necessary by this method to adjust the pressure until the indicating point was at a fixed position. A reading correct to two decimal places could be obtained with this instrument in about five minutes. The temperature of the air used for calibrating the balance should, of course, be known, and then, if the other determinations were made at a different temperature, a correction could be applied.

#### CIV.—*Some New Derivatives of Mesitylene and $\psi$ -Cumene.*

By CHARLES STANLEY GIBSON.

THE investigation of the chemical constituents of certain fractions of Edeleanu oil obtained from Borneo petroleum (compare Jones and Wootton, T., 1907, **91**, 1148) has led to the isolation of hitherto undescribed derivatives of mesitylene and  $\psi$ -cumene. As very little information concerning the chemical behaviour of these hydrocarbons is contained in the literature, it is considered desirable to describe the work which has now been done on these substances.

The most interesting of the new compounds described in the present communication are the dinitro-sulphonic acids of mesitylene and  $\psi$ -cumene, together with their reduction products. Rose (*Annalen*, 1872, **164**, 65) obtained a mononitro-sulphonic acid of mesitylene,  $C_6HMe_3(NO_2)SO_3H \cdot \frac{1}{2}H_2O$ , by dissolving mesitylene-sulphonic acid in well cooled fuming nitric acid. He also described certain of its salts, and this appears to be the only nitro-sulphonic acid of mesitylene hitherto known. No nitro-sulphonic acid of  $\psi$ -cumene appears to have been described previously.

The reduction of dinitromesitylenesulphonic acid under the condition described in the paper leads to the formation of a *diaminomesitylenesulphonic acid*; whereas the reduction of a *dinitro- $\psi$ -cumene-5-sulphonic acid* leads to the formation of a *mononitromonoamino- $\psi$ -cumene-5-sulphonic acid* and also the fully reduced compound, *diamino- $\psi$ -cumene-5-sulphonic acid*. The nitroamino- $\psi$ -cumene-5-sulphonic acid is formed when the reduction of the dinitro-acid is not carried to completion. When the reduction of dinitromesitylenesulphonic acid is not carried to completion, the diamino-sulphonic acid is formed and unchanged dinitro-sulphonic acid is left. From a comparison of the formulae of dinitromesitylenesulphonic acid and dinitro- $\psi$ -cumene-5-sulphonic acid, and from the fact that the former does not appear to yield easily a half-reduced acid, it appears that the constitution of the mononitromonoamino- $\psi$ -cumene-5-sulphonic acid is most likely 6-nitro-3-amino-2:4:5-trimethylbenzenesulphonic acid.

For the investigation considerable quantities of mesitylenesulphonic acid and of  $\psi$ -cumene-5-sulphonic acid were necessary, and methods of preparation of these compounds somewhat more convenient than those previously described (Jacobsen, *Annalen*, 1888, **146**, 95) have been devised.

## EXPERIMENTAL.

*Preparation of Mesitylenesulphonic Acid.*

To determine how far the method of sulphonation adopted was successful, the sulphonation product of the hydrocarbon was isolated as the sodium salt. The pure hydrocarbon (85 c.c.) was stirred at 55°, and 85 c.c. of sulphuric acid (D 1.84) run in fairly rapidly and the whole kept at 55° during two hours. The mixture was diluted with water and treated at 90° with lime in quantity sufficient to neutralise the excess of sulphuric acid, and with sodium carbonate to neutralise the sulphonic acid. After filtering from the calcium sulphate, the solution was evaporated, and the sodium salt of mesitylenesulphonic acid was obtained in almost quantitative yield. It is conveniently recrystallised from boiling water.

The almost pure acid is most conveniently obtained directly by allowing the sulphonated mixture to cool and adding a weight of ice equal to that of the sulphuric acid used. On keeping, mesitylenesulphonic acid crystallises out in theoretical quantity. It is filtered on cloth and dried on porous plate in a desiccator.

The mesitylenesulphonic acid and its sodium salt were identified by conversion into the sulphonyl chloride and sulphonamide in the usual manner. Mesitylenesulphonyl chloride when recrystallised from a mixture of benzene and light petroleum was obtained in colourless, massive prisms, melting at 56--57°, and mesitylenesulphonamide, recrystallised from aqueous alcohol, was obtained in colourless needles melting at 144°. The latter melting point is somewhat higher than that given by Jacobson (*Annalen*, 1876, **184**, 1857).

*Dinitromesitylenesulphonic Acid,  $C_6Me_3(NO_2)_2SO_3H.4H_2O$ .*

This acid may be prepared either from mesitylenesulphonic acid isolated in the way described above or directly from the hydrocarbon. In preparing it from the sulphonic acid, 60 grams are added gradually with stirring to 72 c.c. of concentrated sulphuric acid (D 1.84). Very little rise of temperature takes place, and this operation is performed at the ordinary temperature. The sulphonic acid does not dissolve completely. The mixture is cooled in ice, the stirring continued, and a mixture of 45 c.c. of nitric acid (D 1.4) and 45 c.c. of concentrated sulphuric acid (D 1.84) is added during about two hours. The temperature at the beginning should not be more than 10°, and this gradually rises to about 35° and then begins to fall. The ice bath is then removed, and the addition of the nitrating acid continued at the ordinary

temperature. The temperature rises to about  $40^{\circ}$  and then falls again. At this point the mixture is heated to  $60^{\circ}$ . The time for the nitration is four hours, and the nitrating acid is run in during about two hours.

The above quantity of nitric acid allows a 25 per cent. excess over the two molecules of nitric acid necessary for the reaction, and before all the nitrating acid has been run in, the colour of the mixture becomes very much paler and solid begins to separate. When the nitration is finished, the mixture is allowed to cool and poured on 250 grams of ice and then stirred until no more nitrous fumes are evolved. The crystalline acid is collected, and may be purified either by crystallisation from a small quantity of hot water, or by dissolving in water and adding half the volume of concentrated sulphuric acid, cooling in ice-water. The solution of the acid should be filtered from the small quantity of trinitromesitylene (m. p.  $232-233^{\circ}$ ), amounting to not more than 4 grams. The yield of the acid is rather more than 90 per cent. of the theoretical quantity.

An almost theoretical yield of dinitromesitylenesulphonic acid can be obtained directly from mesitylene. Sixty grams of mesitylene are sulphonated with 69 c.c. of concentrated sulphuric acid (D 1.84) under the conditions described above, and, after the sulphonation is completed, the mixture is cooled in water and the stirring continued while 81 c.c. of concentrated sulphuric acid are added during half an hour. The mixture is then cooled in ice, and the nitrating acid, 60 c.c. of nitric acid mixed with 60 c.c. of concentrated sulphuric acid of the same strengths as before, is added under precisely the same conditions as in the case of the previous preparation. It was found that 5 per cent. of the hydrocarbon is converted into the trinitro-compound; apart from this the yield of the acid is theoretical.

*Dinitromesitylenesulphonic acid* crystallises from its concentrated solution in hot water in large, very pale yellow plates; it contains four molecules of water of crystallisation, but slight decomposition sets in on heating before all the water of crystallisation is expelled (Found, by titration with barium hydroxide solution, M.W. = 357.4, 359.9;  $H_2O = 20.9$ . \*  $C_9H_{10}O_7N_2S_4H_{12}O$  requires M.W. = 362.5;  $H_2O = 19.9$  per cent.).

*Dinitromesitylenesulphonyl Chloride*,  $C_6Me_3(NO_2)_2SO_2Cl$ .

This is prepared in the usual way from the almost anhydrous acid by the action of phosphorus pentachloride. It is readily soluble in benzene, but much less so in light petroleum. It is con-

\* Decomposition had set in.

veniently recrystallised from benzene containing half its volume of light petroleum. It is obtained in almost colourless, long, soft needles melting at  $169-170^{\circ}$  (Found: C=34.9; H=3.12.  $C_9H_9O_6N_2ClS$  requires C=35.0; H=2.94 per cent.).

*Dinitromesitylenesulphonamide*,  $C_6Me_3(NO_2)_2 \cdot SO_2 \cdot NH_2$ .

This derivative is prepared by the action of concentrated ammonia solution on the acid chloride. On crystallisation from hot alcohol, in which it is readily soluble, it is obtained in long, silky needles melting at  $228-229^{\circ}$  (Found: C=37.6; H=3.88.  $C_6H_{11}O_6N_3S$  requires C=37.4; H=3.83 per cent.).

*Salts of Dinitromesitylenesulphonic Acid.*

*Sodium Salt*,  $C_6Me_3(NO_2)_2 \cdot SO_3Na \cdot 4H_2O$ .—This salt was obtained from the acid by accurate titration with standard sodium hydroxide solution. It was crystallised three times from water, in which it is very readily soluble. The salt appears to be amorphous. On allowing the concentrated aqueous solution to remain, extremely soluble, colourless, flat plates separate. On long keeping or on stirring, these change into colourless, silky needles which are much less readily soluble than the plates. It is impossible to collect the plates in the ordinary way, as they change spontaneously in the air into what appears to be the other modification. The change from one form into the other can be readily observed under the microscope (Found:  $H_2O=18.85$ .  $C_9H_9O_7N_2SNa \cdot 4H_2O$  requires  $H_2O=18.76$  per cent. Found: Na=7.50.  $C_9H_9O_7N_2SNa$  requires Na=7.36 per cent.).

*Ammonium Salt*,  $C_6Me_3(NO_2)_2 \cdot SO_3 \cdot NH_4$ .—This salt is easily obtained by the action of ammonia solution on the acid. It can be recrystallised from water, and when the aqueous salt is allowed to evaporate spontaneously, the salt is obtained in colourless, thin plates. On drying in air the substance is anhydrous (Found, by titration with N/10-sodium hydroxide,  $NH_4=6.0, 6.0$ .  $C_9H_{13}O_7N_2S$  requires  $NH_4=5.9$  per cent.).

The *calcium salt*,  $[C_6Me_3(NO_2)_2 \cdot SO_3]_2Ca \cdot 3H_2O$ , is prepared by the action of calcium carbonate on the acid, and can be crystallised from water, in which it is readily soluble. The salt is deposited from its aqueous solution in colourless prisms, which effloresce in air. The crystalline substance loses the whole of its water of crystallisation on keeping in a vacuum over concentrated sulphuric acid. The water of crystallisation was determined by allowing the substance to attain constant weight over sulphuric acid in a vacuum (Found:  $H_2O=8.04$ .  $C_{18}H_{18}O_{14}N_4S_2Ca \cdot 3H_2O$  requires  $H_2O=8.04$  per cent.).



Found: Ca=6.54, 6.47.  $C_{15}H_{18}O_{14}N_4S_2Ca$  requires Ca=6.48 per cent.).

*Barium Salt*,  $[C_6Me_3(NO_2)_2SO_3]_2Ba \cdot 3\frac{1}{2}H_2O$ .—This was obtained in a precisely similar way to the calcium salt. It is readily soluble in water, from which it was twice recrystallised. In appearance it is very similar to the calcium salt (Found:  $H_2O$ =8.35; Ba=17.64; N=7.1, 7.2.  $C_{15}H_{18}O_{14}N_4S_2Ba \cdot 3\frac{1}{2}H_2O$  requires  $H_2O$ =8.1; Ba=17.65; N=7.2 per cent.).

Of the other salts of dinitromesitylenesulphonic acid, the *magnesium* salt is worth mentioning. It can be obtained by precipitation, using a soluble magnesium salt and a soluble salt of the acid. Although the salt has not been further investigated yet, it was at once seen that it is much less readily soluble than the corresponding salt of dinitro-*ψ*-cumene-5-sulphonic acid, and this fact has often been made use of in testing for the presence of the mesitylene acid.

*Diaminomesitylenesulphonic Acid*,  $C_6Me_3(NH_2)_2 \cdot SO_3H$ .

The reduction of dinitromesitylenesulphonic acid can be successfully carried out by the usual methods. In most of the experiments, iron and a minimum quantity of acetic acid have been used, but the reduction by means of ferrous carbonate has also been found satisfactory. Two typical experiments may be described.

Ten grams of the dinitro-acid are exactly neutralised with *N*-sodium hydroxide solution, and water is added until the volume of the solution is about 100 c.c. Twenty grams of cleaned and ground iron borings are placed in a round bottomed flask provided with an air condenser; 30 c.c. of water and 1 c.c. of glacial acetic acid are poured into the flask and allowed to boil gently for about twenty minutes. After this time the boiling solution of the sodium dinitrosulphonate is added slowly from the top of the condenser. The flask is shaken from time to time, and when all the solution has been added, the whole is allowed to boil gently for about one and a-half hours. The most convenient way to obtain the pure acid at once is to add sodium hydroxide equivalent to the acetic acid used for the reduction, and filter the hot solution and wash the residue with a little water. To the filtrate and washings is added hydrochloric acid equivalent to the original dinitro-acid and to the sodium hydroxide added before filtering. The yield is 100 per cent.

Twenty-one grams of dinitromesitylenesulphonic acid are treated with the calculated quantity of standard sodium hydroxide solution, and dissolved in a boiling solution of 77 grams of anhydrous sodium carbonate dissolved in 250 c.c. of water. To the boiling solution is

added slowly 200 grams of crystallised ferrous sulphate dissolved in a litre of water. The mixture is kept boiling and stirred continuously. As soon as all the ferrous sulphate solution has been added, the solution is filtered while still hot, and the filtrate evaporated and then acidified with hydrochloric acid equivalent to the amount of dinitro-acid originally taken. The diamino-acid is at once precipitated in almost theoretical quantity, and is practically pure.

*Diaminomesitylenesulphonic acid*, obtained in either of the above ways, is a colourless, microcrystalline substance insoluble in all the usual organic solvents, including acetic acid. It decomposes without melting. For most purposes it is unnecessary to purify the acid as obtained in the ways described above. For analysis it was purified by dissolving in sodium hydroxide solution, filtering, and adding hydrochloric acid equivalent to the alkali hydroxide. The acid was then washed with warm water (Found: C=47.0; H=6.18.  $C_9H_7O_5N_2S$  requires C=46.9; H=6.13 per cent.).

#### *Sulphonation of $\psi$ -Cumene.*

$\psi$ -Cumene is conveniently sulphonated to  $\psi$ -cumene-5-sulphonic acid under precisely the same conditions as those described above for the preparation of mesitylenesulphonic acid. The yield is quantitative. It should, however, be observed that the whole of the sulphonic acid is not precipitated on dilution, as is the case with mesitylenesulphonic acid, only 75 per cent. of the sulphonic acid being so obtained. The remainder may be conveniently isolated as the calcium salt.

$\psi$ -Cumene-5-sulphonic acid and its calcium salt were identified by converting them into the acid chloride and amide. Quantitative yields of these derivatives were obtained in the usual manner.  $\psi$ -Cumene-5-sulphonyl chloride crystallised from light petroleum ether in large, colourless prisms melting at  $62^\circ$ , and  $\psi$ -cumene-5-sulphonamide, prepared from the chloride and crystallised from alcohol, was obtained in colourless needles melting at  $180$ – $181^\circ$ .

#### *Dinitro- $\psi$ -cumene 5-sulphonic Acid, $C_9H_6(NO_2)_2SO_3H \cdot 4H_2O$ .*

The isolation of this acid is not quite so easy as that of the corresponding mesitylene compound. As in the former case, it may be prepared either from  $\psi$ -cumene-5-sulphonic acid or from the hydrocarbon itself. For the purpose of this investigation the acid was generally prepared from the hydrocarbon.

Sixty grams of  $\psi$ -cumene were sulphonated under the conditions described above, and the sulphonation mixture, while still being

stirred, was mixed during half an hour with 81 c.c. of concentrated sulphuric acid. To this mixture, cooled in ice, was added a mixture of 60 c.c. of nitric acid (D 1.48, that is, 78 grams of  $\text{HNO}_3$  instead of the theoretical quantity, 63 grams) and 60 c.c. of concentrated sulphuric acid during two and a-half hours, and the whole stirred for a further two and a-half hours. By this time the mixture had thickened considerably, and by pouring on 540 grams of ice, 40 grams of the acid were precipitated. The filtrate was then treated with an equal volume of hot brine and allowed to crystallise slowly, when the sodium salt was deposited in fairly pure condition. It may be washed with brine, in which it is almost insoluble. The total yield of the dinitro-sulphonic acid and of its sodium salt is 80 per cent. of the theoretical.

A very convenient method of working up the nitration product was to dilute the nitration mixture, then add sodium hydroxide equivalent to the amount of hydrocarbon taken, and completely neutralise with calcium hydroxide at  $90^\circ$ . After filtering from the calcium sulphate and concentrating the filtrate to crystallisation, the sodium salt was obtained. When it was desired to obtain the pure acid in maximum quantity, the nitration mixture was completely neutralised with calcium hydroxide, and the calcium salt isolated in the usual manner, from which the acid was easily obtained.

*Dinitro- $\psi$ -cumene-5-sulphonic acid* may be conveniently recrystallised from dilute hydrochloric acid, and is easily obtained pure. It crystallises in almost colourless, glistening, radiating crystals, which contain four molecules of water of crystallisation (Found: C=30.4; H=4.93,  $\text{NO}_2$ , from  $\text{SnCl}_2$  required for reduction, =25.1; M.W., by titration with  $N/10\text{-NaOH}$ , =363.8.  $\text{C}_9\text{H}_{10}\text{O}_7\text{N}_2\text{S}_4\text{H}_2\text{O}$  requires C=29.8; H=5.01;  $\text{NO}_2$ =25.4 per cent. M.W.=362.3).

The preparation of dinitro- $\psi$ -cumene-5-sulphonic acid from  $\psi$ -cumene-5-sulphonic acid is carried out under the same conditions as those for the preparation of dinitromesitylenesulphonic acid from the corresponding compound. It is necessary, however, to bear in mind that only part of the product is obtained as the crystalline acid, and that the remainder must be isolated as the sodium or calcium salt under the conditions described above. During the nitration of either  $\psi$ -cumene or of  $\psi$ -cumene-5-sulphonic acid, a small quantity of trinitro- $\psi$ -cumene is always formed. This was identified by recrystallising from alcohol, when it separated in very pale yellow needles, melting at  $185^\circ$ .

*Dinitro- $\psi$ -cumene-5-sulphonyl Chloride and 5-Sulphonamide,*  
 $C_6Me_3(NO_2)_2 \cdot SO_2Cl$  and  $C_6Me_3(NO_2)_2 \cdot SO_2 \cdot NH_2$ .

These derivatives are obtained from the acid or the sodium salt in the usual manner.

The *chloride* crystallises from hot benzene in hard nodules. It is somewhat difficult to obtain quite free from a slight brown colour. It melts and decomposes at  $190-191^\circ$ .

The *amide* is readily soluble in hot alcohol, and crystallises from this solvent in small, glistening needles, which usually have a slight brown colour on cooling. It melts and blackens at  $244-245^\circ$  (Found: C = 37.6; H = 4.02.  $C_9H_{11}O_6N_2S$  requires C = 37.4; H = 3.83 per cent.).

*Salts of Dinitro- $\psi$ -cumene-5-sulphonic Acid.*

*Sodium Salt.*—This is prepared in the way described above or by neutralisation of the acid with standard sodium hydroxide. It is obtained in colourless nodules, which are readily soluble in hot water and somewhat sparingly so in the cold solvent. The salt gradually loses water on keeping in the air (Found, after twenty-four hours, N = 7.54.  $C_9H_9O_7N_2SNa \cdot 3H_2O$  requires N = 7.65 per cent. After one week, loss = 6.84, 6.51.  $C_9H_9O_7N_2SNa \cdot 1H_2O$  requires 5.45 per cent.).

It thus appears that the substance after remaining for some time in ordinary air contains rather more than one molecule of water of crystallisation. The anhydrous salt was analysed (Found: Na = 7.13.  $C_9H_9O_7N_2SNa$  requires Na = 7.36 per cent.).

*Magnesium Salt,*  $[C_6Me_3(NO_2)_2SO_3]_2Mg \cdot 4H_2O$ .—This salt, which is much more readily soluble than the corresponding salt of dinitromesitylenesulphonic acid, may be conveniently obtained by adding a saturated solution of magnesium sulphate to the diluted solution produced in the preparation of the acid. After two recrystallisations from its concentrated aqueous solutions, it is obtained in pale yellow, small needles (Found:  $H_2O$  = 10.77; N = 7.9;  $MgO$  = 3.42.  $C_{12}H_{15}O_{14}N_4S_2Mg \cdot 4H_2O$  requires  $H_2O$  = 10.68; N = 8.3;  $MgO$  = 3.60 per cent.).

*Barium Salt,*  $[C_6Me_3(NO_2)_2SO_3]_2Ba \cdot 4H_2O$ .—This salt was prepared by adding a solution of barium chloride to a neutral solution of the ammonium salt. The salt was at once precipitated, and after being washed free from excess of barium chloride formed small, colourless needles (Found:  $H_2O$  = 9.1; N = 7.2; Ba = 17.4.  $C_{12}H_{15}O_{14}N_4S_2Ba \cdot 4H_2O$  requires  $H_2O$  = 9.15; N = 7.1; Ba = 17.4 per cent.).

*Diamino- $\psi$ -cumene-5-sulphonic Acid*,  $C_6Me_3(NH_2)_2 \cdot SO_3H$ .

This acid is prepared from the corresponding dinitro-acid most conveniently by reduction with iron and acetic acid, as described for the preparation of diaminomesitylenesulphonic acid. The yield obtained was 93 per cent. of the theoretical. Like the mesitylene acid it is practically insoluble in all the usual organic solvents, including acetic acid. It decomposes without melting. Unlike the mesitylene acid it has been found impossible to obtain the acid free from colour; even after the most careful purification it still possesses a slight red colour, but analysis showed that the acid was pure (Found: C=46.7; H=6.30.  $C_9H_{14}O_3N_2S$  requires C=46.9; H=6.13 per cent.).

*Nitroamino- $\psi$ -cumene-5-sulphonic Acid*,  $C_6Me_3(NO_2)(NH_2) \cdot SO_3H$ .

During the reduction of the neutral solution of the dinitro-sulphonic acid prepared from Edeleanu oil by means of iron and acetic acid it was found that, on isolation of the reduction product in the usual way, a portion was identical with diamino- $\psi$ -cumene-5-sulphonic acid and, of course, insoluble in water, whilst a smaller portion was found to be capable of recrystallisation from hot water and not identical with any of the amino- or nitro-acids previously described. Further, indications of the formation of a new acid were obtained during the estimation of the amount of dinitro-sulphonic acids in solution by means of stannous chloride solution. It was therefore determined to try the effect of reducing sodium dinitro- $\psi$ -cumene-5-sulphonate by means of stannous chloride in quantity calculated to produce a mononitromonoamino-sulphonic acid. In these circumstances an almost theoretical amount of what is probably 6-nitro-3-amino-2:4:5-trimethylbenzenesulphonic acid was obtained.

Sodium dinitro- $\psi$ -cumene-5-sulphonate (6.2 grams) was heated in an atmosphere of carbon dioxide with 50 c.c. of a solution of stannous chloride made by dissolving 263 grams of crystallised stannous chloride in 130 c.c. of concentrated hydrochloric acid and making up to one litre. After titration with standard iodine solution it was found that 6 grams of anhydrous sodium salt required 54.5 c.c. of the above stannous chloride solution for reduction to a mono-amino-acid. The reduction was effected in a flask which was heated during two hours in a water-bath. The product was strongly acidified with concentrated hydrochloric acid, and, after cooling, the material was collected and crystallised from boiling water, in which it is readily soluble, but it is sparingly soluble in the cold.

It crystallises in yellowish-brown needles which have no melting point (Found: C=41.4; H=4.56.  $C_6H_{12}O_3N_2S$  requires C=41.5; H=4.65 per cent.). Work on the above and other derivatives of mesitylene and  $\psi$ -cumene is being continued.

The above work was carried out in the University Chemical Laboratory, Cambridge, and I wish to record my thanks to Professor Sir William Pope, F.R.S., for placing much of the material employed at my disposal and for his advice and help. I have also to express my thanks to the Directors of the Asiatic Petroleum Company for their permission to publish the work.

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### IV.—*Studies on Hypophosphorous Acid. Part I.* *Its Ionisation Equilibria.*

By ALEC DUNCAN MITCHELL.

In the course of some investigations on the velocity of various reductions by means of hypophosphorous acid, it was found that the reactions were catalysed by hydrogen ions; and as these reactions involved the production of mineral acids, such as hydrochloric and hydriodic acids, it was decided to investigate the ionisation of hypophosphorous acid in the presence of hydrochloric acid, in order to obtain data for more precise mathematical analysis of the reactions in question.

Although the catalysis of methyl acetate is in some respects an inferior method to those involving conductivity or hydrogen-ion potential methods for problems of this nature, yet it was chosen in this case as being more comparable with the catalytic reactions concerned. Moreover, one of the chief disadvantages of the method, namely, the slight uncertainty as to the effect of neutral molecules, has been overcome to a large extent by the method of calculating the results.

Many empirical formulæ have been advanced, from time to time, to connect the degree of ionisation of "strong" acids with the dilution in such a way as to give a constant analogous to that obtained for weak acids by Ostwald, but none of these is capable of predicting the equilibria which obtain when one of the ions is present in excess. It has been put forward as a working hypo-

thesis that, in a mixture of two strong electrolytes, each is ionised to the same degree as it would be if present alone in a solution having the same total ion concentration as the mixture. Arrhenius, for instance (*Zeitsch. physikal. Chem.*, 1888, 2, 285; 1899, 31, 218), used it in connexion with "neutral salt action," although it is often at variance with the requirements of the law of mass action; and Bray and Hunt, more recently (*J. Amer. Chem. Soc.*, 1911, 33, 781), have found it to hold with considerable accuracy in the case of sodium chloride and hydrochloric acid mixtures.

When the values of the Ostwald function  $\alpha^2/(1-\alpha)v$  were worked out for hypophosphorous acid, they were found to decrease arithmetically as the dilution  $v$  increased geometrically (over the range  $v=8$  to  $v=2048$ ). This connexion was expressed by the empirical formula

$$\alpha^2/(1-\alpha)v = 0.1015 - \frac{1}{3} \log v.$$

(All logarithms in this communication are to the base 10.)

In table I are shown under the various columns:

$v$  = dilution.

$\lambda$  = molecular conductivity.

$\alpha$  = degree of dissociation.

$K_0$  = the value of the Ostwald expression.

$K_a$  = the value of the above empirical expression.

$K$  = the value of  $\alpha^2/(1-\alpha)v + \frac{1}{3} \log v$ , which is practically a constant.

$[H']$  = the concentration of the hydrogen ions in the equilibria.

$I$  = the total ionic concentration.

$K_r$  = the value of van't Hoff's equation  $\alpha^{1.5}/(1-\alpha)\sqrt{v} = K_r$ .

TABLE I.

$v$ .	$\lambda$ .	$\alpha$ .	$K_0$ .	$K_a$ .	$K$ .	$[H']$ .	$I$ .	$K_r$ .
1	—	—	—	0.1015	—	—	—	—
2	140	0.360	0.1012	0.0929	—	0.1800	0.360	0.238
4	172	0.442	0.0876	0.0843	—	0.1105	0.221	0.263
8	207	0.532	0.0757	0.0757	0.1015	0.0665	0.1330	0.293
16	245	0.630	0.0670	0.0671	0.1014	0.0394	0.0788	0.330
32	281	0.722	0.0587	0.0585	0.1017	0.02256	0.0451	0.391
64	312	0.802	0.0508	0.0499	0.1014	0.01255	0.0251	0.454
128	335	0.861	0.0417	0.0413	0.1019	0.00672	0.0134	—
256	352	0.905	0.0336	0.0327	0.1024	—	—	0.566
512	361	0.928	0.0234	0.0241	0.1008	—	—	—
1024	367	0.944	0.0154	0.0155	0.1014	—	—	—
2048	368.3	0.948	0.0082	0.0069	0.1028	—	—	—
$\infty$	389	—	—	—	—	—	—	—

Van't Hoff's expression obviously fails, and Rudolphi's is still less applicable. Concordant values cannot be obtained for the constant in Partington's equation. Kraus and Bray's expression

$(1-\alpha)v = K + D(\alpha, v)^m$ , applies over the same range as  $K_r$ , while

$D=0.217$  and  $m=0.10$ , but this gives a negative value of  $K=-0.090$ .

It was hoped that the value of  $\alpha$  could be found mathematically from the known value of the total ion concentration, or, of course, from the hydrogen-ion concentration, which is one half of it. This hope has been partly fulfilled, but the formula cannot apply to solutions more concentrated than  $v=8$ , beyond which the empirical formula fails. Nevertheless, the value of  $\alpha$  as found agrees with that demanded by the total ion hypothesis up to the highest concentrations studied, which are considerably beyond the limit mentioned above.

Obviously the empirical formula fails before  $v=3600$ , where it gives negative values.

The data on which the values of  $\alpha$  in the table are based are Ostwald's conductivity measurements at  $25^\circ$ , but the molecular conductivity at infinite dilution is not given by him, and had to be obtained from a consideration of several values for the  $H_2PO_2'$  ion combined with the value 347 for the hydrogen ion, which is the value now generally adopted (Kendall, T., 1912, 101, 1283).

The data selected as being most consistent were:

(a) Bredig (*Zeitsch. physikal. Chem.*, 1894, 13, 191), from the sodium salt, finds the value for  $H_2PO_2'$  at  $25^\circ$  to be 41.8.

(b) Bredig (*ibid.*) finds 105.3 for the barium salt, whence  $H_2PO_2'=39.5$ .

(c) Arrhenius (*Zeitsch. physikal. Chem.*, 1889, 4, 99), using old units, gives a value for hypophosphorous acid which by conversion becomes 389, and this is the value adopted.

Hypophosphorous acid is one of the few acids which show a maximum of equivalent conductivity with increasing temperature; it occurs at  $55^\circ$  for this acid. This has been investigated by Arrhenius (*loc. cit.*), who refers it to anomalous values for the heat of neutralisation, and, therefore, for the heat of ionisation, which is negative instead of positive, as is normally the case.

Although hypophosphorous acid is described in the literature as a weak acid (Arrhenius, *ibid.*, and Abegg's "Theory of Electrolytic Dissociation" in Ahrens' Sammlung), yet it appears to be a "strong" acid according to more recent convention, which regards "intermediate" acids those having ionisation constants of 0.001 to 0.01.

#### EXPERIMENTAL.

The determinations of the velocity constants were carried out in a thermostat at  $25 \pm 0.05^\circ$ . The methyl acetate was freshly distilled and free from acid. The hypophosphorous acid was an old



stock of Kahlbaum's chemically pure acid, which showed only a trace of oxidation to phosphorous acid, so that its titre was almost identical with either methyl-orange or phenolphthalein as indicator, but as the latter indicates the second hydrogen ion of phosphorous acid, the titre with this indicator was used in all cases where differences were involved, and the actual strength of the solution was based on its titre with methyl-orange as indicator.

Baryta solutions, prepared by diluting a  $N/4$ -solution to one-half, one-fourth, or one-eighth of its strength, were used for titrations. Steamed and dried Jena-glass bottles of 500 c.c. capacity were employed. The required amount of water was run in by 100, 50, and 25 c.c. pipettes, and 10 c.c. were drawn out to allow for the subsequent addition of that volume of ester. The necessary volumes of  $N/2$ - or  $N/8$ -acids were added, and the volume before the addition of the ester was 390 c.c. in each case. The general procedure was as in routine methods. Thus all experiments were strictly comparative.

Several titrations were carried out between fifty and seventy minutes after mixing, and were then adjusted to that for sixty minutes by making use of the velocity found for the early stages; the mean of these was used as zero time. In the stronger acid solutions, the final value was attained in ten days, and was employed in the equation  $kt = \log x_{\infty} - \log(x_{\infty} - x)$ . This equation is only strictly applicable in the early stages of the reaction, since it fails to take into account the reverse reaction between alcohol and acid. The more accurate velocity equation is  $dx/dt = k'(a - x) - k''x^2$ , where  $a$  represents the whole amount of ester (which is of the order of 5 per cent. greater than  $x_{\infty}$ ), and where  $k'$ , like  $k$ , embodies the large and practically constant value of the molecular concentration of water. Hence, remembering that  $k'(a - x_{\infty}) = k''x_{\infty}^2$ , one obtains the integrated expression

$$k't \frac{2a - x_{\infty} - x}{x_{\infty}} = \log \frac{x(a - x_{\infty}) + ax_{\infty}}{a(x_{\infty} - x)} = \log \left[ \frac{x_{\infty}}{x_{\infty} - x} + \frac{x(a - x_{\infty})}{a(x_{\infty} - x)} \right].$$

From this it can be shown that the measurements should not extend beyond the first third of the reaction, in order that the change in the ratio  $k/k'$  may not exceed one-third per cent., and thus be within the experimental error. Within the prescribed limits,  $k/k'$  is equal to 1.055, and the relative error caused by using the simpler formula may be ignored.

In tables IIa and IIb, under the heading  $k$ , are shown the constants obtained; they are in all cases the mean of several values agreeing usually within 1 per cent., so that the error in  $k$  does not exceed one-half per cent., and is generally much less.

In each case, a formula enclosed in square brackets indicates the molecular concentration of the molecule or ion in question.

$\alpha$  represents the degree of dissociation of the acid concerned in table IIA, and of the hypophosphorous acid in IIB.

$\alpha$ , and  $K$ , are the values of  $\alpha$  and  $K$  in solutions of hypophosphorous acid alone which have the same hydrogen-ion (or total ion) concentration as the mixed solution to which they relate. Both were taken from curves plotted from the data in table I.  $K$ , (found) is calculated from the experimental results by a formula which is developed later.

The values of  $k \times 10^6 / [H^+]$  in the case of hydrochloric acid are obviously affected by the undissociated molecules, which possess about double the catalytic activity of the hydrogen ions (Snethlage, *Zeitsch. Elektrochem.*, 1902, **18**, 539, and Dawson, T., 1913, **103**, 2139). Lundén (*Zeitsch. physikal. Chem.*, 1904, **49**, 189) puts the activity of the hydrogen ions of hydrochloric acid in ester-catalyses equal to  $[H^+](1 + 0.34[H^+])$ , and application of this formula gives the more consistent values under its heading.

The undissociated hypophosphorous acid molecules have a much smaller effect, but may account for the high value for its strongest

TABLE IIA.

$[H_2PO_2]$	$[HCl]$	$k \times 10^6$	$\alpha$	$[H^+]$	$k \times 10^6 / [H^+]$	$[H^+](1 + 0.34[H^+])$	$k \times 10^6$
—	0.125	350	0.914	0.1143	3060	2950	Mean 2930
—	0.0625	174	0.934	0.0584	2990	2920	
—	0.03125	87.1	0.950	0.0297	2930	2910	
—	0.01563	44.5	0.963	0.01505	2960	2940	
0.125	—	199.0	0.532	0.0665	(2990)	Mean 2925	
0.0625	—	115.0	0.630	0.0394	2920		
0.03125	—	66.0	0.722	0.02255	2925		
0.01563	—	36.7	0.802	0.01225	2925		

TABLE IIB.

$[H_2PO_2]$	$[HCl]$	$k \times 10^6$	Due to		$\alpha$	$K$	$K$
			$H_2PO_2$	$[H_2PO_2] / [H^+]$	(found)	(found)	(found)
0.125	0.01563	228	183.5	0.0626	0.0776	0.501	0.503
0.125	0.03125	262	175.1	0.0598	0.0895	0.478	0.477
0.125	0.0625	337	163	0.0556	0.1150	0.445	0.436
0.125	0.125	490	140	0.0478	0.1625	0.382	0.377
0.0625	0.01563	151	106.5	0.03635	0.0514	0.582	0.580
0.0625	0.03125	187	99.9	0.0311	0.0638	0.546	0.541
0.0625	0.0625	266	92	0.0214	0.0898	0.502	0.476
0.0625	0.125	422	72	0.0246	0.1389	0.393	0.400
0.03125	0.01563	104	59.5	0.0203	0.05535	0.650	0.648
0.03125	0.03125	140.6	53.5	0.01825	0.0479	0.584	0.592
0.03125	0.0625	220	46.0	0.0157	0.0741	0.502	0.510
0.03125	0.125	389	39.0	0.0133	0.1276	0.426	0.416
0.01563	0.01563	78.6	32.1	0.01095	0.0260	0.701	0.698
0.01563	0.03125	117.0	29.9	0.01025	0.0400	0.656	0.626
0.01563	0.0625	200	26	0.00887	0.0673	0.568	0.528
0.01563	0.125	370	20	0.00683	0.1211	0.437	0.426

solution, where they constitute nearly half of the acid. As the acid does not give a definite affinity constant, the formula of Taylor (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, 2, Nos. 34, 35, 37) cannot be applied to estimate this effect, but indicates that it is very small.

#### Discussion of Results.

In order to avoid the difficulty due to the uncertainty as to the effect of undissociated hydrochloric acid molecules, in each case the value for the appropriate concentration of hydrochloric acid (as shown in table IIA) is subtracted from the constant obtained, and the remainder is attributed to the hydrogen ions derived from the hypophosphorous acid. If this remainder is divided by 2930, the mean value of  $k \times 10^6 \div [H']$ , one obtains the concentration of the corresponding hydrogen and  $H_2PO_2'$  ions. (The experimental error is considerably magnified by this subtraction, and especially so in those cases where the hydrochloric acid ions are considerably in excess of those of the hypophosphorous acid.) The total hydrogen-ion concentration is obtained by adding that due to the hydrochloric acid alone. One assumes implicitly that the ionisation of the hydrochloric acid is not depressed, and, although this cannot be rigidly true, a comparison of the ionisation values of the two acids shows that the effect on the stronger acid would be negligible compared with that on the weaker acid. Moreover, as the molecules of the hydrochloric acid possess a catalytic activity, the total activity of the hydrochloric acid would be slightly increased, and so tend to lead to slightly high values for  $\alpha$ .

The values for the ionisation of hydrochloric acid were selected from a mass of discordant data which vary by 3 per cent. or more in the literature on the subject, but the recent careful determinations by Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, 33, 781) were used, by interpolation, as they agree well with the means of all others and also with those of Goodwin and Haskell (*Physical Rev.*, 1904, 19, 369), which, however, were carried out at 18°.

It is clearly seen that  $\alpha$  for hypophosphorous acid in any mixture approximates closely to  $\alpha_1$ , the degree of ionisation it would have if present alone in the same concentration of hydrogen ions.

If we consider one mole of hypophosphorous acid in  $v$  litres of water, which also contain  $h$  equivalents of extraneous hydrogen ions, we have  $\frac{\alpha(\alpha+h)}{(1-\alpha)v} = K_1$ , and, considering a solution of one mole alone at a dilution  $v_1$ , such that the concentration of hydrogen ions is the same as in the first solution,  $\alpha_1$  being its degree

of ionisation, we have  $\frac{a_1^2}{(1-a_1)v_1} = 0.1015 - \frac{1}{3.5} \log v_1 = K_1$ , but  $a_1 = a$ , as already found, and, since the hydrogen-ion concentrations are equal,  $\frac{a+h}{v} = \frac{a_1}{v_1}$ . Therefore  $v_1 = v \frac{a}{a+h}$  and

$$K_1 = \frac{a(a+h)}{(1-a)v} = \frac{a_1^2}{(1-a_1)v_1} = K_1 = 0.1015 - \frac{1}{3.5} \log \frac{va}{a+h} = 0.1015 - \frac{1}{3.5} \log \frac{a}{[H]}.$$

This formula enables us to derive from the experimentally determined  $a$  a value of  $K_1$ , which is seen to agree well with that found from a graph for a hypophosphorous acid solution having the same hydrogen-ion concentration, when this does not exceed that of a  $N/8$ -solution (that is, 0.0665).

$K_1$  is not shown, as it is very susceptible to experimental error.

Attempts have been made, so far unsuccessfully (except possibly for phosphorous acid), to apply an analogous formula to other fairly strong acids, and also to seek for a theoretical significance.

#### Conclusions.

1. The hypothesis that, in a mixture of two electrolytes, each is ionised to the same extent as it would be if present alone in a solution having the same concentration of ions, has been found to apply to hypophosphorous acid in presence of hydrochloric acid.
2. The empirical formula  $a^2/(1-a)v = 0.1015 - \frac{1}{3.5} \log_{10} v$  holds for hypophosphorous acid in dilutions down to  $v=8$ .
3. In virtue of these two facts, the ionisation equilibria of hypophosphorous acid in the presence of extraneous hydrogen ions is represented in dilute solutions by

$$[H^+][H_2PO_2^+]/[H_3PO_2] = 0.1015 - \frac{1}{3.5} \log_{10} a^2/[H^+].$$

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CVI.—*Derivatives of Gallic Acid. Part I.\* Synthesis of 4-Hydroxy-3:5-dimethoxyphthalic Acid.*

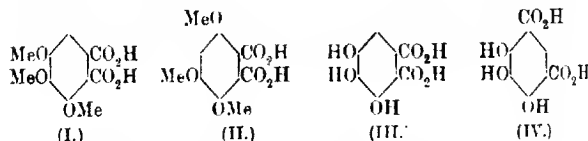
By RUPCHAND LILARAM ALIMCHANDANI and ANDREW NORMAN MELDRUM.

Hydroxy- and methoxy-phthalic acids are often obtained as degradation products of naturally occurring substances, such as dyes and alkaloids. Windaus, for instance, studied the alkaloids colchicine, which contains three methoxy-groups and a hydroxy-group, and colchicine, which contains four methoxy-groups; by oxidising colchicine, which he regards as the methyl ether of colchicine, he obtained a trimethoxyphthalic acid (*Sitzungsber. Heidelberger Akad. Wiss.*, 1910, 1; 1914, Abh. 18). Feist had previously studied columbamine, which contains four methoxy-groups and a hydroxy-group. By methylating columbamine, he obtained the methyl ether of columbamine, which on oxidation gave a trimethoxyphthalic acid (*Arch. Pharm.*, 1907, **245**, 586). Recently, Feist and Sandstedt have again studied this derivative (*Arch. Pharm.*, 1918, **256**, 1). The following table shows the melting points observed for the substances:

	Acid.	Anhydride.
Windaus .....	175—176°	143—144°
Feist .....	200°	—
Feist and Sandstedt .....	185°	128°

Feist and Sandstedt, in spite of the differences in melting point, conclude that their trimethoxyphthalic acid is identical with that obtained by Windaus from colchicine.

There are two possible trimethoxyphthalic acids, I and II, and, obviously, synthetic work on these acids is valuable. Feist converted pyrogalloldicarboxylic acid into its trimethyl ether, and on comparison found it to be different from his compound. The value of the comparison is now doubtful. Pyrogalloldicarboxylic acid may have the constitution III or IV. It had always been assumed

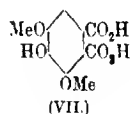
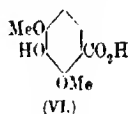
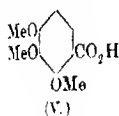


\* A preliminary note on the subject of this paper was read at the Indian Science Congress, in the Chemistry Section, January, 1919.

to be III, in view of the fact that it had been synthesised from gallic acid; recently, Hemmelmayr (*Monatsh.*, 1917, **38**, 77) obtained it, using gallic acid and potassium hydrogen carbonate, in almost theoretical yield. Voswinkel and de Weerth had already suggested that in this synthesis migration of the carboxyl group of gallic acid must occur; the resulting acid does not give an anhydride, and they concluded that it has the constitution IV (*Ber.*, 1912, **45**, 1242).

The authors undertook the synthesis of 3:4:5-trimethoxyphthalic acid (I) by a method which should leave no doubt as to the constitution of the product. After this had been accomplished, they learnt that Bargellini and Molina had carried out the same synthesis, and by the same method (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 146). There is, however, a considerable difference in the details, since the authors obtained derivatives of syringic acid (VI), whilst Bargellini and Molina did not. These derivatives of syringic acid are important in connexion with columbamine, and perhaps with colchicine, both of which alkaloids conceivably contain a syringic acid residue. By methylation, the authors were able to obtain a trimethoxyphthalic acid (I) which is identical with Bargellini and Molina's acid.

The constitution I and VII for the respective phthalic acids can be regarded as established in view of (1) the synthetic method employed, (2) the fact that the acids give anhydrides, (3) the fact that the acids can be reconverted into the substances V and VI, respectively, from which they were synthesised.



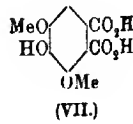
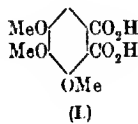
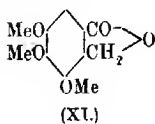
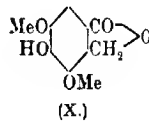
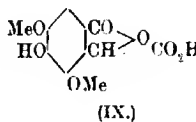
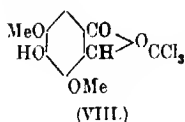
The two substances I and VII are genuine derivatives of gallic acid. Compound I (m. p. 176–177°) is different from the trimethyl ether of pyrogalloldicarboxylic acid (Feist, m. p. 195°), which therefore is not a true gallic acid derivative. Pyrogalloldicarboxylic acid is therefore IV, and when this acid is synthesised from gallic acid, the carboxyl group of gallic acid must be displaced, as Voswinkel and de Weerth suggested.

The method employed, which is due to Fritsch, consists in the condensation of a hydroxybenzoic acid with chloral, leading to the formation of a trichloromethylphthalide; the trichloromethyl group is eliminated, and the resulting phthalide is oxidised to a dicarboxylic acid, which can be only an orthophthalic acid (*Annalen*, 1897, **296**, 358; 1898, **301**, 360; see also T., 1911, **99**, 1712).

Fritsch recommends that in carrying out the condensation with chloral, the hydroxybenzoic acid should be used in the form of its methoxy-ester. This is not always necessary, for the authors find that the trimethyl ether of gallic acid and even gallic acid undergo the condensation, yielding trichloromethylphthalides.

3:4:5-Trimethoxybenzoic acid (V) and chloral give a substance which has not the composition that was at first expected. On investigation, it was found that the sulphuric acid employed as the condensing agent hydrolyses the trimethoxybenzoic acid and produces syringic acid (VI). The original method of obtaining syringic acid from trimethoxybenzoic acid was to hydrolyse by means of hydrobromic acid (Graebe and Martz, *Annalen*, 1905, **340**, 220). Bogert and Isham (*J. Amer. Chem. Soc.*, 1914, **36**, 519) introduced the use of fuming sulphuric acid. For some time the authors were in doubt as to the acid they obtain, using ordinary sulphuric acid, for it has not the aromatic odour which Bogert and Isham ascribe to syringic acid. The authors therefore satisfied themselves that the substance is syringic acid by preparing its methyl ester, the acetyl derivative of the methyl ester, and, by oxidation, 3:5-dimethoxy-*p*-benzoquinone. Hence the use of ordinary sulphuric acid in making syringic acid has the advantage of not giving rise to the impurity, possessing an aromatic odour, which Bogert and Isham obtained.

Whether trimethoxybenzoic acid, or its methyl ester, or syringic acid is condensed with chloral, the product is the same, namely, 4-hydroxy-3:5-dimethoxy-2-trichloromethylphthalide (VIII). Syringic acid gives the larger and purer yield. In place of VIII. Bargellini and Molina obtained the corresponding trimethoxy-compound; they carried out the reaction using trimethoxybenzoic acid methyl ester. So far as the authors can judge, the difference does not depend on the use of the ester; it is probably due to a difference in the sulphuric acid employed, or to the higher temperature at which the reaction was carried out in India, or to both these causes.



The trichloromethylphthalide, on hydrolysis, gives 4-hydroxy-3:5-dimethoxyphthalide-2-carboxylic acid (IX). This, when heated, loses carbon dioxide and gives 4-hydroxy-3:5-dimethoxyphthalide (X). From this, on methylation, 3:4:5-trimethoxyphthalide (XI) is obtained, and this, on oxidation, gives rise to 3:4:5-trimethoxyphthalic acid (I), which readily gives an anhydride. When this anhydride is dissolved in sulphuric acid and the solution is poured into water, the product is 4-hydroxy-3:5-dimethoxyphthalic acid (VII), which also readily gives an anhydride. This acid is the oxidation product of the phthalide (X), from which, however, the authors were unable to obtain it by direct oxidation. Boiling with hydrochloric acid converts I into V and VII into VI.

## EXPERIMENTAL.

*Salts of 3:4:5-Trimethoxybenzoic Acid.*

Trimethoxybenzoic acid was prepared according to Graebe and Martz's method (*loc. cit.*). The following hitherto undescribed salts were prepared and analysed.

*Sodium Salt.*—The acid was dissolved in sodium hydroxide solution, and a hot concentrated solution of the alkali was added. The sodium salt gradually crystallised in long, rectangular plates; it was collected, washed quickly with water, crushed on a porous tile, and dried in a desiccator (Found: Na=9.84.  $C_{10}H_{11}O_5Na$  requires Na=9.83 per cent.).

*Potassium Salt.*—This was obtained in the same manner as the sodium salt. It crystallises in plates (Found: K=15.97.  $C_{10}H_{11}O_5K$  requires K=15.60 per cent.).

*Lead Salt.*—The acid was dissolved in very dilute ammonia, the excess of ammonia evaporated, and a dilute solution of neutral lead acetate was added. The lead salt crystallises in silky needles (Found: Pb=32.52.  $(C_{10}H_{11}O_5)_2Pb$  requires Pb=32.91 per cent.).

*Syringic Acid (VI).*

3:4:5-Trimethoxybenzoic acid (25 grams) was dissolved in sulphuric acid (100 c.c. of 36–98 per cent.), and, after about twenty-four hours, the liquid was poured into water (200 c.c.), when syringic acid was precipitated in silky needles (19 grams). It sinters at 204° and melts at 206–207°.

Small amounts were converted into methyl syringate (hydrated: m. p. 84–86°), methyl acetylsyringate (m. p. 131°), and 3:5-dimethoxy-*p*-benzoquinone (m. p. 255°).



*4-Hydroxy-3:5-dimethoxy-2-trichloromethylphthalide* (VIII).

Syringic acid (7 grams), chloral hydrate (9 grams), and sulphuric acid (50 c.c.) were mixed together, and, on vigorous shaking, the solids dissolved. After about forty-eight hours, the liquid was poured on ice. A white solid separated, which was collected and washed with water, the yield being 10 grams. The substance crystallises from methyl alcohol in truncated, rectangular plates melting at  $172-173^{\circ}$  (Found: Cl = 32.50.  $C_{11}H_8O_5Cl_3$  requires Cl = 32.50 per cent.).

The *acetyl* derivative of the above compound was prepared, using acetic anhydride and a few drops of concentrated sulphuric acid. It crystallises from absolute alcohol in small clusters of prisms melting at  $139^{\circ}$  (Found: Cl = 28.78.  $C_{13}H_{11}O_6Cl_3$  requires Cl = 28.80 per cent.).

*Sodium Compound*.—It was possible to prepare the sodium derivative of the above trichloro compound without hydrolysing it. The substance was dissolved in ice-cold dilute sodium hydroxide solution, and concentrated sodium hydroxide solution (ice-cold) was added. A yellow *sodium* compound separated, which was rapidly collected, dried on porous tile, and then analysed (Found: Na = 7.08. Calc.: Na = 6.6 per cent.).

*4-Hydroxy-3:5-dimethoxyphthalide-2-carboxylic Acid* (IX).

The trichloro compound (15 grams) was boiled with a solution of sodium hydroxide (15 grams) in water (125 c.c.). The substance first turned yellow, then gradually dissolved, and the solution became dark. On acidifying this solution, the free acid was obtained in white needles (11 grams). For analysis, it was crystallised from acetic acid, and finally from water.

The substance contains water of crystallisation; it was found to effloresce at the ordinary temperature and to lose water completely at  $100-110^{\circ}$ . It then melts and decomposes at  $187^{\circ}$  (Found:  $H_2O = 6.47$ .  $C_{11}H_8O_7 \cdot 2H_2O$  requires  $H_2O = 6.62$  per cent.).

The anhydrous substance was analysed (Found: C = 52.16; H = 4.23.  $C_{11}H_6O_7$  requires C = 52.00; H = 3.94 per cent.).

The *calcium* salt crystallises with one molecule of water. When heated, it decomposes, for concordant figures for the water of crystallisation could not be obtained [Found: Ca = 6.98.  $(C_{11}H_6O_7)_2 \cdot Ca \cdot H_2O$  requires Ca = 7.08 per cent.].

The acid, on titration with standard alkali, gave no definite result, as there was no sharp neutralisation point.

*4-Hydroxy-3:5-dimethoxyphthalide (X).*

The phthalidecarboxylic acid (14 grams), along with naphthalene (40 grams), was heated to 200–210°, until the evolution of carbon dioxide ceased. Naphthalene was then removed in a current of steam, and the solution of the phthalide in water was filtered. It crystallises in prismatic needles melting at 144°. For analysis, it was recrystallised from ethyl acetate (Found: C=57.19; H=4.97.  $C_{10}H_{10}O_3$  requires C=57.15; H=4.76 per cent.).

Oxidation of this substance did not give a definite product.

*3:4:5-Trimethoxyphthalide (XI).*

The phthalide just described (5 grams) was dissolved in sodium hydroxide (15 grams) dissolved in water (100 c.c.). To this, dimethyl sulphate (20 c.c.) was added in small amounts, and the mixture was heated. On acidification, needle-shaped crystals were obtained, which were recrystallised from ethyl acetate for analysis. The substance melts at 135–136° (Bargellini and Molina give 134–135°) (Found: C = 59.1; H = 5.64. Calc.: C = 58.94; H = 5.36 per cent.).

*3:4:5-Trimethoxyphthalic Acid (I).*

3:4:5-Trimethoxyphthalide (8 grams) was dissolved in excess of dilute potassium hydroxide, and to the cold solution potassium permanganate (8 grams) dissolved in water (260 c.c.) was added. After about forty-eight hours, the manganese dioxide was filtered off, and the bluish-green colour of the filtrate was removed by means of sulphurous acid. The solution was then evaporated to small bulk, filtered, and acidified, when 3:4:5-trimethoxyphthalic acid crystallised in white, rhombic plates. For analysis, it was recrystallised from water, when it melted and decomposed at 176–177° (Bargellini and Molina give 174°) (Found: C=51.46; H=4.84. Calc.: C=51.56; H=4.70 per cent. Equivalent found: 128.3. Calc.: 128).

*3:4:5-Trimethoxyphthalic Anhydride.*

The anhydride was prepared by heating the phthalic acid carefully at its melting point. The product crystallises from benzene in clusters of needles melting at 147° (Bargellini and Molina give 143°). (Equivalent found: 118.8. Calc.: 119.)

A mixture of the trimethoxyphthalic acid with concentrated

hydrochloric acid was boiled under reflux for an hour. On cooling, crystals of trimethoxybenzoic acid (V) were obtained.

*4-Hydroxy-3:5-dimethoxyphthalic Acid (VII).*

3:4:5-Trimethoxyphthalic anhydride (4 grams) and sulphuric acid (20 c.c. of 96—98 per cent.) were mixed, when the anhydride dissolved easily. After three days, the solution was poured on ice, when a crystalline substance separated. On recrystallisation from water, it melted and decomposed at 225—227° (Found: C=49.35; H=4.21.  $C_{10}H_{10}O_7$  requires C=49.58; H=4.13 per cent.).

The results of titration with standard alkali were untrustworthy, as there was no sharp neutralisation point.

*4-Hydroxy-3:5-dimethoxyphthalic Anhydride.*

The anhydride was obtained by heating the phthalic acid just described at its melting point. The product crystallises from toluene in needles melting at 177—179° (Found: C=53.6; H=3.9.  $C_{10}H_8O_6$  requires C=53.6; H=3.6 per cent.).

*Syringic Acid from 4-Hydroxy-3:5-dimethoxyphthalic Acid.*

A mixture of the phthalic acid (0.5 gram) and concentrated hydrochloric acid (20 c.c.) was boiled under reflux for about four hours. The hot solution was filtered, and white, silky needles separated from the filtrate. The substance was recrystallised, and was found to be syringic acid (VI).

A study of the various substances formed by the interaction of chloral and gallic acid is almost concluded.

MADHAVLAL RANCHHODLAL SCIENCE INSTITUTE,

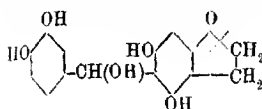
AHMEDABAD, INDIA.

[Received, October 24th, 1913.]

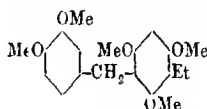
CVII.—*The Constitution of Catechin.\* Part I.*

By MAXIMILIAN NIERENSTEIN.

KOSTANECKI and Lampe (*Ber.*, 1907, **40**, 720) have shown that when catechin tetramethyl ether is reduced with metallic sodium and alcohol, an oil (desoxyhydrocatechin tetramethyl ether) is formed, which on further methylation yields a crystalline pentamethyl derivative, and they regarded this as 2:4:6:3':4'-pentamethoxy-3-ethylidiphenylmethane (II). Its production was con-

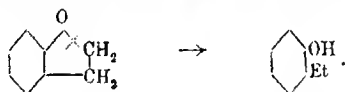


(I.)

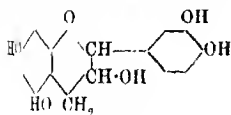


(II.)

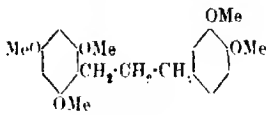
sidered by them as being strong evidence in favour of their coumaran formula for catechin (I), especially as Alexander (*Ber.*, 1892, **25**, 2409) had previously found that coumaran itself may be reduced under the same conditions to *o*-ethylphenol:



Ryan and Walsh (*Sci. Proc. Roy. Dublin Soc.*, 1916, **15**, 113) have pointed out that these deductions are in no way conclusive, since the reactions described by Kostanecki and Lampe can also be explained on the basis of the original chroman formula (III) proposed by A. G. Perkin and Yoshitake (*T.*, 1902, **81**, 1172). Ryan and Walsh have consequently suggested formula IV as an alternative to Kostanecki and Lampe's formula (II) for the methylated reduction product.



(III.)

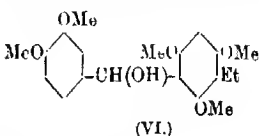
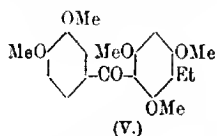


(IV.)

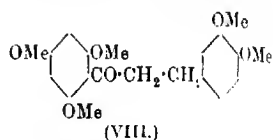
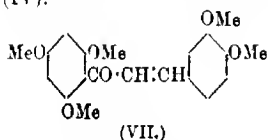
With the view of deciding between the chroman and coumaran

\* For a complete summary of the literature see Perkin and Everest, *The Journal Organic Colouring Matters*, 1918.

formula,\* Ryan and Walsh attempted the synthesis of 2:4:6:3':4'-pentamethoxy-3-ethyldiphenylmethane (II), but owing to the lack of material they were unable to accomplish it. Both this substance and 3:4:2':4':6'-pentamethoxy- $\alpha$ -diphenylpropane (IV) have now been synthesised according to the following schemes: 2:4:6:3':4'-pentamethoxy-3-ethylbenzophenone (V) was reduced to 2:4:6:3':4'-pentamethoxy-3-ethyldiphenylcarbinol (VI), which on further reduction gave 2:4:6:3':4'-pentamethoxy-3-ethyldiphenylmethane (II). 2:4:6-Trimethoxyphenyl



3:4-dimethoxystyryl ketone (VII) was first reduced to 2:4:6-trimethoxyphenyl 3:4-dimethoxy- $\beta$ -phenylethyl ketone (VIII), and subsequently to 3:4:2':4':6'-pentamethoxy- $\alpha$ -diphenylpropane (IV).



As will be seen from the following summary of the melting points and mixed melting points of these substances, neither 2:4:6:3':4'-pentamethoxy-3-ethyldiphenylmethane (II) nor 3:4:2':4':6'-pentamethoxy- $\alpha$ -diphenylpropane (IV) is identical with the methylated reduction product described by Kostanecki and Lampe:

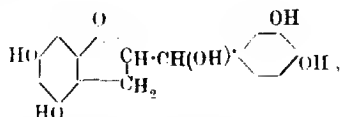
Melting point of Kostanecki and Lampe's product, 83–84°.

Melting point of 2:4:6:3':4'-pentamethoxy-3-ethyldiphenylmethane (II), 91–92°.

Mixed m. p. with Kostanecki and Lampe's product, 49–65°.

Melting point of 3:4:2':4':6'-pentamethoxy- $\alpha$ -diphenylpropane (IV), 87–88°.

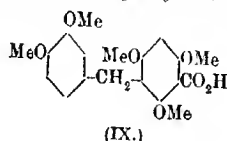
\* It should be noted that the coumaran formula:



which has also been considered by Kostanecki and Lampe (*loc. cit.*) would also lead to 3:4:2':4':6'-pentamethoxy- $\alpha$ -diphenylpropane (IV).

Mixed m. p. with Kostanecki and Lampe's product, 61—69°.

During the course of the present investigation, it was found that Kostanecki and Lampe's methylated reduction product, which has the empirical formula \*  $C_{26}H_{26}O_6$ , yields on oxidation the acid,  $C_{19}H_{22}O_7$ , which melts at 150—151°. As may be seen, this oxidation is accompanied by the loss of one carbon atom, and this was found to be a general reaction in the case of compounds,†  $R \cdot CH_2 \cdot CH_3$ , which yield the corresponding acids,  $R \cdot CO_2H$ . Similarly, 2:4:6:3':4'-pentamethoxy-3-ethyldiphenylmethane (II) gives 2:4:6:3':4'-pentamethoxydiphenylmethane-3-carboxylic acid,



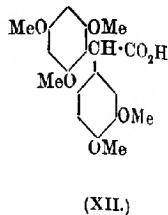
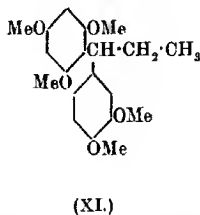
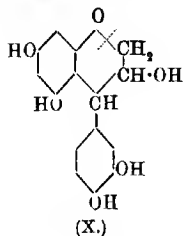
(IX), which melts at 108°. 3:4:2':4':6'-Pentamethoxy- $\alpha$ -diphenylpropane (IV), on the other hand, is recovered unchanged, which still further accentuates the differences between Kostanecki and Lampe's methylated reduction product and 2:4:6:3':4'-pentamethoxy-3-ethyldiphenylmethane (II) and 3:4:2':4':6'-pentamethoxy- $\alpha$ -diphenylpropane (IV).

These observations indicate that on reduction and subsequent methylation, the coumaran or the chroman nucleus yields the product,  $C_{18}H_{22}O_5 \cdot CH_2 \cdot CH_3$ , from which, on oxidation, the acid,  $C_{18}H_{21}O_5 \cdot CO_2H$ , is produced. The only coumaran formula in agreement with these facts is that proposed by Kostanecki and Lampe (I), but, as previously pointed out, this formula is untenable. By a slight modification of Perkin and Yoshitake's chroman formula (III), the observations recorded in this paper become, however, readily explicable. Thus, considering catechin to be represented by formula X, Kostanecki and Lampe's methyl-

\* The empirical formula given by Kostanecki and Lampe (*Ber.*, 1907, 40, 2524) is  $C_{26}H_{26}O_6$ , which requires C = 66.3; H = 7.2 per cent. They calculate and find, however, correctly for  $C_{26}H_{26}O_5$  (Found: C = 69.36; H = 7.51. Calc.: C = 69.29; H = 7.59 per cent.). I have also analysed this substance and find C = 69.1; H = 7.6 per cent. as required by  $C_{26}H_{26}O_5$ .

† The products used were: 2:4-dimethoxyethylbenzene, 2:4-dihydroxyethylbenzene and 2:3:4-trihydroxyethylbenzene. They were prepared from the corresponding ketones (compare Clemmensen, *Ber.*, 1913, 46, 1837; 1914, 47, 51, 681). Of these substances 2:4-dimethoxyethylbenzene has so far not been described. It is an oil boiling at 238–241°/767 mm. (Found: C = 72.0; H = 8.6— $C_{10}H_{14}O_2$  requires C = 72.3; H = 8.4 per cent.). The acids obtained on oxidation: dimethyl- $\beta$ -resorcylic,  $\beta$ -resorcylic and pyrogallol-carboxylic acid respectively, had the correct melting points. Mixed melting points showed no depression.

ated reduction product becomes 3:4:2':4':6'-pentamethoxy- $\alpha$ -diphenylpropane (XI), and the acid obtained from it 3:4:2':4':6'.



pentamethoxydiphenylacetic acid (XII). This acid (XII) has been prepared by the Grignard reaction from carbon dioxide and 3:4:2':4':6'-pentamethoxydiphenylmethyl chloride, and was found to be identical in every respect with the acid obtained by the oxidation of Kostanecki and Lampe's methylated reduction product.

#### EXPERIMENTAL.

##### 2:4:6:3':4'-Pentamethoxy-3-ethyldiphenylmethane (II).

The 2:4:6:3':4'-pentamethoxy-3-ethylbenzophenone (V) required for the reduction was prepared by Ryan and Walsh's method (*loc. cit.*). It crystallised from dilute alcohol in needles melting at 127—129°, whereas Ryan and Walsh give 123—124° (Found: C=66.5; H=6.9. Calc.: C=66.7; H=6.7 per cent.).

##### 2:4:6:3':4'-Pentamethoxy-3-ethyldiphenylcarbinol (VI).

A solution of 5 grams of the ketone in 70 c.c. of alcohol is heated for nineteen hours on a water-bath with an aqueous solution of 15 grams of potassium hydroxide and 25 grams of zinc dust. The solution is filtered while hot, and the zinc dust extracted several times with alcohol. The filtrate is concentrated to about 20 c.c., and 170 c.c. of water are added. The precipitate crystallises from dilute alcohol in needles, which melt at 112°. The carbinol is soluble in the usual organic solvents, with the exception of light petroleum. With concentrated sulphuric acid, it yields a deep red solution (Found\*: C=66.1; H=7.3.  $C_{20}H_{26}O_6$  requires C=66.3; H=7.2 per cent.).

By digesting with acetic anhydride and anhydrous sodium acetate, the *acetyl* derivative is easily prepared. It crystallises from alcohol in small cubes, which melt at 109—110°. Since the

\*Dried over phosphoric oxide in a vacuum.

melting points of the carbinol and that of the acetyl derivative are practically identical, it is to be noted that mixtures melted 12–17° below the melting points of the compounds (Found\*: C=65.4; H=7.2.  $C_{22}H_{22}O_7$  requires C=65.3; H=6.9 per cent.).

The *methyl* derivative is prepared by the action of methyl sulphate and alkali on an alcoholic solution of the carbinol. It crystallises from methyl alcohol in prismatic needles, which melt at 94°. Diazomethane does not methylate this carbinol (compare Geake and Nierenstein, T., 1915, 107, 1491; Dean and Nierenstein, T., 1916, 109, 596) (Found\*: C=66.7; H=7.7.  $C_{21}H_{20}O_8$  requires C=67.0; H=7.4 per cent.).

2:4:6:3':4'-Pentamethoxy-3-ethyldiphenylmethane (II).

Three grams of the carbinol dissolved in 100 c.c. of alcohol are reduced with 12 grams of metallic sodium. The solution is heated on a water-bath for twelve hours, when all the sodium disappears. After removal of the alcohol with steam, and cooling, a resinous mass is deposited, the alcoholic solution of which leaves, on evaporation, an oil, which becomes semi-solid on keeping over phosphoric oxide. This product is again dissolved in a little alcohol and precipitated with water, and this process of purification is repeated until a dry specimen dissolves in concentrated sulphuric acid without any coloration. It crystallises from a mixture of benzene and alcohol (2:1) in small, prismatic needles, which melt at 91–92°. The substance is soluble in the usual organic solvents, with the exception of light petroleum. The alcoholic solution shows a pale blue fluorescence. The average yield is 64 per cent. of the theoretical. Two different preparations were used for analysis (Found †: C=69.5, 69.1; H=7.9, 8.1.  $C_{20}H_{20}O_5$  requires C=69.3; H=7.5 per cent.).

2:4:6:3':4'-Pentamethoxydiphenylmethane-3-carboxylic Acid (IX).

To a suspension of 1.4 grams of the diphenylmethane derivative (II) in 50 c.c. of 2*N*-potassium hydroxide, 50 c.c. of 2*N*-potassium permanganate are added, and the solution is heated on a water-bath for five and a-half hours. The cold solution is filtered, acidified with dilute sulphuric acid, and extracted several times with ether. The dried ethereal extract leaves a residue, which crystallises from water in silky needles melting at 108°, carbon

\* Dried over phosphoric oxide in a vacuum.

† Dried over paraffin in a vacuum.



dioxide being evolved. The yield is 0.6 gram (Found\*: C=62.9; H=6.3.  $C_{20}H_{22}O_7$  requires C=63.0; H=6.1 per cent.).

A solution of 0.46 gram of the acid in dry ether gives, on treatment with an ethereal solution of diazomethane (from 7 c.c. of nitrosomethylurethane), a quantitative yield of the *methyl* ester. It crystallises from benzene in prismatic needles melting at 81°, carbon dioxide being evolved. On warming with dilute alkali, the original acid is regenerated (Found†: C=63.5; H=6.3.  $C_{20}H_{24}O_7$  requires C=63.8; H=6.4 per cent.).

3:4:2':4':6'-Pentamethoxy- $\alpha$ -diphenylpropane (IV).

Tutin and Caton (T., 1910, 97, 2067) have prepared the 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone (VII) required for the reduction by the action of finely divided sodium on an ethereal solution of veratraldehyde and trimethoxyacetophenone. Both this method and that described by Göschke and Tambor (Ber., 1912, 45, 186) for the preparation of similar substances were tried, with the result that the following method was finally adopted. To a warm alcoholic solution of 3 grams of veratraldehyde and 3.8 grams of trimethoxyacetophenone, 10 grams of a 50 per cent. solution of alcoholic potassium hydroxide are slowly added. The mixture is allowed to remain for forty-eight hours, diluted with water, and the alcohol removed by distillation with steam. On cooling, a viscous mass is formed, which is washed several times with water, and subsequently dissolved in alcohol and precipitated with water. It crystallises from dilute alcohol in yellow, prismatic needles, which melt at 84–85°; after remaining over paraffin in a vacuum for some time, the melting point rises to 117–118°. These two melting points are in agreement with those given by Tutin and Caton, who find 85° for the product containing one molecule of alcohol and 117.5° for the alcohol-free product.

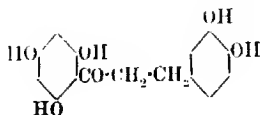
2:4:6-Trimethoxyphenyl 3:4-Dimethoxy- $\beta$ -phenylethyl Ketone<sup>‡</sup> (VIII).

Bargellini's method (Gazzetta, 1911, 41, ii, 442; 1912, 42, ii, 425) for the reduction of methoxyphenyl styryl ketones was

\* Dried over phosphoric oxide in a vacuum.

† Dried over paraffin in a vacuum.

‡ The preparation of this substance is of some interest, since A. G. Perkin (T., 1905, 87, 405) has also tentatively suggested the following formula for catechin:



and to give a colourless product, whereas the reduction with acetic acid and zinc dust gives a slightly coloured substance. The former process may be conveniently carried out in the apparatus devised by Ellis and Gardner (*Biochem. J.*, 1918, **12**, 72) for the reduction of cholesterol. The product crystallises from alcohol in needles, which melt at  $91^{\circ}$ , the average yield being 92 per cent. of the theoretical. It is soluble in the usual organic solvents. The alcoholic solution is turned faintly pink by the addition of ferric chloride (Found\*: C=66.8, 66.4; H=7.2, 6.9.  $C_{20}H_{24}O_6$  requires C=66.7; H=6.7 per cent.).

### 3:4:2':4':6'-Pentamethoxy- $\alpha$ -diphenylpropene (IV).

Three grams of 2:4:6-trimethoxyphenyl 3:4-dimethoxy- $\beta$ -phenylethyl ketone dissolved in 100 c.c. of alcohol are heated for six hours with 15 grams of metallic sodium. The greater part of the alcohol is removed by evaporation, and the alcoholic solution diluted with water. The precipitate which separates crystallises from dilute alcohol in small needles melting at  $87-88^{\circ}$ . The average yield is 74 per cent. of the theoretical (Found: C=69.5, 69.2; H=7.8.  $C_{20}H_{20}O_5$  requires C=69.3; H=7.5 per cent.).

### Oxidation of Kostanecki and Lampe's Methylated Reduction Product to 3:4:2':4':6'-Pentamethoxydiphenylacetic Acid (XII).

Twelve grams of Kostanecki and Lampe's product suspended in 50 c.c. of a 20 per cent. solution of potassium hydroxide in water are oxidised on a boiling-water bath for four hours with 12 grams of potassium permanganate dissolved in 200 c.c. of water. The solution is filtered while hot, and, after cooling, is acidified with dilute sulphuric acid. The dark-coloured precipitate thus obtained is crystallised several times from water, animal charcoal being

In this case 2:4:6-trimethoxyphenyl 3:4-dimethoxy- $\beta$ -phenylethyl ketone (III), which melts at  $91^{\circ}$ , should be identical with catechin pentamethyl ether. The latter substance has been prepared by Kostanecki and Lampe by the action of methyl sulphate (*Ber.*, 1906, **39**, 4011). They give its melting point as  $95^{\circ}$ . The author (*Annalen*, 1913, **396**, 197), who has obtained this substance by the action of diazomethane, finds its melting point to be  $84-86^{\circ}$ . Catechin pentamethyl ether was therefore also prepared according to Kostanecki and Lampe's method, and was found to melt at  $84-86^{\circ}$ . (Found: C=66.3; H=6.9. Calc.: C=66.5; H=6.8 per cent.). This suggests the melting point given by Kostanecki and Lampe is a clerical error. The boiling points of mixtures of catechin pentamethyl ether and 2:4:6-trimethoxyphenyl 3:4-dimethoxy- $\beta$ -phenylethyl ketone showed depressions of  $21^{\circ}$ , thus proving that these two substances are not identical, which consequently excludes the above formula for catechin.

\* Dried over phosphoric oxide in a vacuum.

† Dried at  $110^{\circ}$ .

used, when long, hairy, colourless needles are obtained, which melt at  $150-151^{\circ}$ , carbon dioxide being evolved. The ethereal extract of the original filtrate also gives a small amount of a crystalline product, which, on being recrystallised from water, melts at  $150-151^{\circ}$ . The substance is soluble in alcohol, ethyl acetate, or acetic acid, but insoluble in chloroform, benzene, or light petroleum. The yield is about 70 per cent. of the theoretical. Two different preparations were analysed (Found\*: C=63.2, 62.8; H=6.6, 6.7. M.W. †=374, 368, 364.  $C_{19}H_{22}O_7$  requires C=63.0; H=6.1 per cent. M.W.=362).

The sodium salt is prepared in the usual way by means of sodium hydrogen carbonate. It crystallises from water in microscopic, prismatic needles, which char and decompose at  $328-333^{\circ}$ , without melting (Found: Na=10.1.  $C_{18}H_{21}O_7Na$  requires Na=9.4 per cent.).

The methyl ester, prepared by the action of an ethereal solution of diazomethane (from 14 c.c. of nitrosomethylurethane) on 1 gram of the acid dissolved in ether, crystallises from alcohol in needles, which melt at  $119^{\circ}$ , carbon dioxide being evolved (Found ‡: C=63.8; H=6.8.  $C_{20}H_{24}O_7$  requires C=63.8; H=6.4 per cent.). On warming with dilute alkali, the acid is regenerated (m. p.  $150-151$ ).

### 3:4:2':4':6'-Pentamethoxydiphenylacetic Acid (XII).

3:4:2':4':6'-Pentamethoxydiphenylmethyl chloride was prepared by heating 8 grams of 3:4:2':4':6'-pentamethoxydiphenylcarbinol§ (Kostanecki and Lampe, *Ber.*, 1906, **39**, 4015) on a water-bath for three hours with 8 grams of thionyl chloride. As much as possible of the unchanged thionyl chloride was distilled off under diminished pressure, the last traces being removed by warming with 3 c.c. of formic acid (compare H. Meyer, *Monatsh.*, 1901, **22**, 428). The residue crystallises from dry benzene in long, prismatic needles, which melt at  $69^{\circ}$ . The yield is 94 per cent.

\* Dried at  $110^{\circ}$ .

† By titration with N/10-potassium hydroxide and phenolphthalein.

‡ Dried over phosphoric oxide in a vacuum.

§ The 3:4:2':4':6'-pentamethoxybenzophenone (Kostanecki and Tambor, *Ber.*, 1906, **39**, 4023) required was prepared by the condensation of phloroglucinol trimethyl ether and veratroyl chloride. The latter substance is described as an oil boiling at  $270-277^{\circ}$  (Kostanecki and Tambor, *loc. cit.* who used phosphorus pentachloride) and as a crystalline solid, melting at  $68-69^{\circ}$  (Ryan and Walsh, *loc. cit.*, who used thionyl chloride). I have prepared veratroyl chloride by both these methods and find that the addition of a small crystal of Ryan and Walsh's substance immediately causes the product prepared by Kostanecki and Tambor's method to solidify. Both these preparations melt at  $68-69^{\circ}$ .

of the theoretical (Found: Cl=10.2.  $C_{18}H_{21}O_5Cl$  requires Cl=9.9 per cent.).

Twelve grams of the chloride dissolved in dry ether (Grignard) are heated on a water-bath with 2 grams of "activated" magnesium (Baeyer, *Ber.*, 1905, **38**, 2759), dry carbon dioxide being passed through the solution for three and a-half hours. The solution turns red and becomes filled with a flocculent, yellow product, which reaches its maximum in about three hours. The ether is evaporated, and the residue first diluted with ice-water and subsequently decomposed with 40 c.c. of carefully cooled concentrated hydrochloric acid. The yellow, brittle solid is warmed with 75 c.c. of a solution consisting of 50 c.c. of concentrated ammonia and 50 c.c. of water, when the greater part dissolves. The filtrate is acidified with dilute sulphuric acid and the precipitate crystallised from water with the aid of animal charcoal. Long, silky needles are obtained, which melt at  $150-151^\circ$ , carbon dioxide being evolved. This melting point is not depressed when the substance is mixed with the acid prepared from Kostanecki and Lampe's methylated reduction product. The yield is 74 per cent. of the theoretical (Found\*: C=62.8; H=6.6. Calc.: C=63.0; H=6.1 per cent.).

An ethereal solution of 1 gram of the acid gives on treatment with ethereal diazomethane (from 13 c.c. of nitrosomethylurethane) the methyl ester previously described. It crystallises from alcohol in needles melting at  $119^\circ$ , and a mixture of the two preparations melts at the same temperature (Found†: C=63.5; H=6.7. Calc.: C=63.8; H=6.4 per cent.). On warming with dilute alkali, the original acid is regenerated (m. p.  $150-151^\circ$ ).

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\* Dried at  $110^\circ$ .

† Dried over paraffin in a vacuum.

CVIII.—*Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part II. The Effect of Position-isomerism and Conjugation on Optical Activity among Aryl Derivatives of Amino- and Bisimino-camphor.*

By BAWA KARTAR SINGH, DALIP SINGH, GURU DUTT, and .  
GOPAL SINGH.

DEVIATIONS from Frankland's rule, as indicated among arylimino-camphor derivatives by Singh and Mazumdar (T., 1919, 115, 566), extend also to the corresponding products of reduction, prepared in the manner described by Forster and Thornley (T., 1909, 95, 942).

The molecular rotatory power of the new derivatives of phenyl-aminocamphor are tabulated below.

TABLE I.

Derivatives of phenylaminocamphor	[M] <sub>D</sub> in chloroform solution.		
	Me(15)	Br(80)	OMe(31)
Ortho.....	179°	235°	272.2°
Meta .....	361	277.6	—
Para.....	265	288.9	186

$o < p < un^* < m$ ,  $o < m < p < un$ ,  $p < o < un$

The value of  $[M]_D$  of phenylaminocamphor is 311°.

\* Unsubstituted.

TABLE II.

Derivatives of phenylaminocamphor	[M] <sub>D</sub> in methyl-alcoholic solution.		
	Me(15)	Br(80)	OMe(31)
Ortho .....	174°	230.2°	146.3°
Meta .....	198	207.9	—
Para .....	158	209.6	—

$p < o < m < un$ ,  $m < p < un < o$ ,  $o < un$ ;

The value of  $[M]_D$  of phenylaminocamphor is 229.8°. The mean temperature of the observations recorded in tables I and II was 16° to 23°.

The following conclusions may be drawn from the data given in tables I and II:

(1) The order of rotatory power as laid down by Frankland is not followed once in the above five cases.

(2) The difference in rotatory powers of *o*- and *p*-tolyl compounds is one and a-half times as large as that in the case of the bromophenyl derivatives in chloroform solution, although bromine is a heavier group than the methyl radicle.

(3) In no case has the para-compound the maximum rotation, whereas the ortho-, meta-, and the unsubstituted compound each has had the maximum rotatory power.

(4) The effect of solvent on the order of rotatory power of position isomerides is remarkable; the *o*-bromophenyl compound has the lowest value in chloroform, whereas it has the highest value in methyl alcohol.

(5) Cohen's rule is only followed in two cases in chloroform solution, but not in the remaining three cases.

It is thus clear that we have as yet no rule which can apply to all the cases hitherto investigated, and the most important point which has emerged from this work is that the nature of the solvent plays a considerable part in the order of rotation of position-isomerides.

Apart from the irregularities which are disclosed when corresponding *o*-, *m*-, and *p*-derivatives are compared with the parent substance, it is found that in the case of derivatives of phenylaminocamphor there is no simple connexion between the nature of the substituting element or group and its influence on rotatory power. In the case of the ortho-compounds, arranged in the order of increasing rotatory power, the sequence of the substituent element or group is  $\text{Me} < \text{Br} < \text{OMe} < \text{H}$  in chloroform solution and  $\text{OMe} < \text{Me} < \text{H} < \text{Br}$  in methyl-alcoholic solution, whilst for meta-compounds the order is  $\text{Br} < \text{H} < \text{Me}$  in chloroform and  $\text{Br} < \text{Me} < \text{H}$  in methyl-alcoholic solution, and for para-compounds  $\text{OMe} < \text{Me} < \text{Br} < \text{H}$  in chloroform and  $\text{Me} < \text{Br} < \text{H}$  in methyl alcohol. It is also clear that there is no simple relation between the nature of solvent and the sequence of the substituent element or group on the order of rotatory power. Similar irregularities have already been pointed out in connexion with the derivatives of phenylaminocamphor (Singh and Mazumdar, *loc. cit.*).

The marked effect of conjugated linkings on the optical rotation of compounds in the series under discussion was shown by Forster and Thorley (*loc. cit.*), particularly in connexion with *p*-phenylene-sisiminocamphor. Similar examples were given by Forster and Spitzer (T., 1919, 115, 889), and it is further emphasised by the following measurements in chloroform:



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weight in 19.9 c.c. of the solvent and examining the solution in a 2-dm. tube within half an hour.

The *ortho*-compound melts at 132–133° (Found: C=79.06; H=9.07.  $C_{17}H_{23}ON$  requires C=79.37; H=8.95 per cent.).

Solvent.	Sub- stance. Gram.	Temper- ature.	Time. Hours.	$\alpha_m$ .	$[\alpha]_D$ .	$[M]_D$ .
Methyl alcohol .....	0.0439	16°	—	+0.30°	+67.9°	+174.0°
"	"	17	38	0.26	58.9	150.4
Chloroform .....	0.0557	17	—	0.39	69.7	179.0
"	"	17	21	0.48	85.7	220.

The *meta*-compound melts at 83–84° (Found: C=79.14; H=9.0 per cent.).

Solvent.	Sub- stance. Gram.	Temper- ature.	Time. Hours.	$\alpha_m$ .	$[\alpha]_D$ .	$[M]_D$ .
Methyl alcohol .....	0.0642	17°	—	+0.48°	+77.5°	+198.1°
"	"	17	14	0.53	83.7	215.1
Chloroform .....	0.0505	17	—	0.71	140.6	361.3
"	"	17	14	0.65	128.7	330.7

The *para*-compound melts at 82–84° (Found: C=79.34; H=8.99 per cent.).

Solvent.	Sub- stance. Gram.	Temper- ature.	Time. Hours.	$\alpha_m$ .	$[\alpha]_D$ .	$[M]_D$ .
Methyl alcohol .....	0.0485	18°	—	+0.30°	+61.5°	+158.1°
"	"	18	20	0.28	57.5	146.8
Chloroform .....	0.0542	17	—	0.56	102.8	264.2
"	"	17	8	0.54	99.2	254.9

*o*, *m*-, and *p*-Bromophenylaminocamphor,  $C_{15}H_{14} \begin{smallmatrix} CH \cdot NH \cdot C_6H_4 \cdot Br \\ \diagdown \\ CO \end{smallmatrix}$ .

These are readily soluble in ether, chloroform, or benzene, sparingly so in methyl alcohol or ethyl alcohol, and insoluble in water; they crystallise from hot alcohol in colourless prisms or needles.

The *ortho*-compound melts at 148° (Found: C=59.51; H=6.21.  $C_{15}H_{14}ONBr$  requires C=59.61; H=6.21 per cent.). The measurements of rotatory power, made as above, showed very slight mutarotation.

Solvent.	Sub- stance. Gram.	Temper- ature.	$\alpha_m$ .	$[\alpha]_D$ .	$[M]_D$ .
Chloroform .....	0.0404	19°	+0.31°	+76.3°	+245°
Methyl alcohol .....	0.0278	19	0.20	71.1	230

The *meta*-compound melts at 95° (Found: C=59.21; H=6.41 per cent.).



The rotatory-power determinations gave the following values without mutarotation:

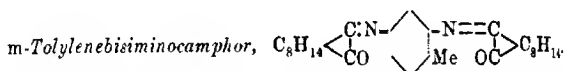
Solvent.	Sub- stance. Gram.	Temper- ature.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Chloroform .....	0.5655	19°	+0.49°	+86.2°	+278°
Methyl alcohol .....	0.0323	19	0.21	64.6	208

The *para*-compound melts at 105° (Found: C=59.21; H=6.35 per cent.).

Solvent.	Sub- stance. Gram.	Temper- ature.	Time. Hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Chloroform .....	0.0532	19°	—	+0.48°	+89.7°	+289°
" .....	"	19	24	0.50	93.5	300
Methyl alcohol .....	0.0359	19	—	0.23	65.1	209
" .....	"	19	24	0.24	67.8	218

For comparison with the foregoing substances, the following measurements were made with phenylaminocamphor:

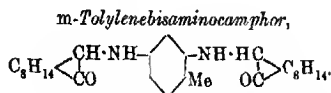
Solvent.	Sub- stance. Gram.	Temper- ature.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Chloroform .....	0.0504	23	+0.65°	+128.3°	+311°
Methyl alcohol .....	0.0555	23	0.53	95	229.8



One molecular proportion of *m*-tolylenediamine hydrochloride and two molecular proportions of camphorquinone were mixed with excess of fused sodium acetate and heated on the water-bath for two hours. The product was cooled, dissolved in a small quantity of alcohol, and precipitated by the addition of water. It crystallises from ether in yellowish-green needles melting at 172° (Found: N=6.69.  $C_{27}H_{34}O_2N_2$  requires N=6.89 per cent.).

It is readily soluble in ethyl alcohol, methyl alcohol, ether, or chloroform, and insoluble in water. The rotatory-power determinations were carried out by dissolving the given weight of the substance in 100 c.c. of the solvent, with the following result, no mutarotation being observed:

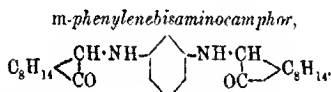
Solvent.	Sub- stance. Gram.	Temper- ature.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Chloroform .....	0.0330	20°	+0.22°	+333.3°	+1393°
Methyl alcohol .....	0.0342	20	0.17	248.5	1038.7



Reduction in this case was effected in the usual way by shaking an ethereal solution of *m*-tolylenebisaminocamphor with zinc dust and 10 per cent. potassium hydroxide in a closed bottle for three hours. The colourless residue left by the ether crystallised from ethyl alcohol in needles melting at  $139^{\circ}$  (Found: C=76.3; H=9.2.  $C_{27}H_{38}O_2N_2$  requires C=76.09; H=9.2 per cent.).

The rotatory-power determinations gave the following values without mutarotation:

Solvent.	Sub- stance. Gram.	Temper- ature.	$\alpha_D$	$[\alpha]_D$	$[M]_D$
Chloroform .....	0.0320	$20^{\circ}$	+0.27°	+83.9°	+354°
Methyl alcohol .....	0.0292	20	0.26	91.6	386

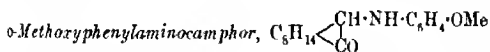


*m*-Phenylenebisaminocamphor (compare Singh and Mazumdar, *loc. cit.*) gave on reduction, as in the last case, *m*-phenylenebisaminocamphor, which crystallised from alcohol in colourless prisms melting at  $163^{\circ}$  (Found: C=76.2; H=8.1.  $C_{26}H_{36}O_2N_2$  requires C=76.4; H=8.4 per cent.).

It is readily soluble in ether or chloroform, sparingly so in ethyl alcohol or methyl alcohol, and insoluble in water.

The rotatory-power determinations gave the following values without mutarotation:

Solvent.	Sub- stance. Gram.	Temper- ature.	$\alpha_D$	$[\alpha]_D$	$[M]_D$
Chloroform .....	0.0250	$20^{\circ}$	+0.38°	+151.2°	+435.5°
Methyl alcohol .....	0.0227	20	0.27	118.3	342.7



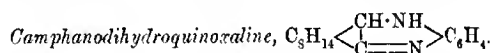
*o*-Methoxyphenylaminocamphor (compare Singh and Mazumdar, *loc. cit.*), when reduced in the usual way, loses its colour, with the formation of *o*-methoxyphenylaminocamphor; this crystallises from alcohol in white needles melting at  $148$ – $149^{\circ}$  (Found:

C=74.03; H=8.67.  $C_{17}H_{23}O_2N$  requires C=74.45; H=8.76 per cent.).

It is readily soluble in chloroform or ether, less so in benzene, acetone, methyl alcohol, or ethyl alcohol, and insoluble in water.

The rotatory-power determinations gave the following values without mutarotation:

Solvent.	Sub- stance. Gram.	Temper- ature.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Methyl alcohol .....	0.2331	20°	+0.25°	+53.6°	+146.3°
Chloroform .....	0.2306	20	0.46	99.7	272.2

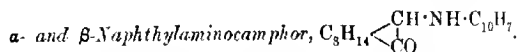


Camphanoquinoxaline was reduced with stannous chloride and concentrated hydrochloric acid by heating for half an hour on the water-bath. On cooling, the stannichloride of camphanodihydroquinoxaline separated as a yellow, granular mass, which was collected, washed with hydrochloric acid, and treated with warm dilute potassium hydroxide, the *camphanodihydroquinoxaline* being extracted with ether; the colourless residue crystallised from hot alcohol in needles melting at 210–215° (Found: C=79.7; H=8.2.  $C_{16}H_{20}N_2$  requires C=80.0; H=8.3 per cent.).

The rotatory-power determinations gave the following values:

Solvent.	Sub- stance. Gram.	Temper- ature.	Time. Hours.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Chloroform .....	0.2276	20°	—	−0.80°	−175.7°	−421.68
„	„	29	20	−0.82	−180.0	−432.0

It is noteworthy that camphanodihydroquinoxaline has a fairly high levorotatory power, whereas the parent substance, camphanoquinoxaline, possesses only a comparatively low dextrorotatory power,  $[M]_D + 68^\circ$  (compare Singh and Mazumdar, *loc. cit.*).

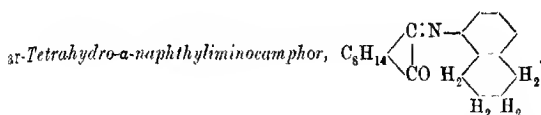


$\alpha$ -Naphthylaminocamphor melted at 163–165°, and was identical with Forster and Spinners' compound (T., 1919, 115, 891). The rotatory-power determinations gave the following values without mutarotation:

Solvent.	Sub- stance. Gram.	Temper- ature.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Methyl alcohol .....	0.3065	16.8°	+0.44°	+71.77°	+210.1°
Chloroform .....	0.2794	18	0.51	91.3	267.5

$\beta$ -Naphthylaminocamphor, also prepared by Forster and Spinner (*loc. cit.*), was obtained in fine, silky needles melting at  $156^{\circ}$ . The rotatory-power determinations gave the following values without mutarotation:

Solvent.	Sub- stance. Gram.	Temper- ature.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Methyl alcohol .....	0.0565	$18^{\circ}$	$+0.71^{\circ}$	$+125.0$	$+366.2^{\circ}$
Chloroform .....	0.0565	18	0.81	142.6	417.8



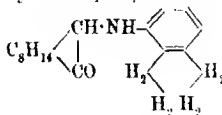
On mixing an alcoholic solution of camphorquinone with an aqueous solution of *ar*-tetrahydro- $\alpha$ -naphthylamine hydrochloride in the presence of excess of sodium acetate, an immediate reaction takes place, with the separation of a dark oil. The mixture is heated under reflux for two hours on the water-bath to complete the reaction. The product is precipitated by the addition of water, and crystallises from dilute alcohol in yellow needles melting at  $132$ – $134^{\circ}$  (Found:  $C=80.93$ ;  $H=8.45$ .  $C_{25}H_{25}ON$  requires  $C=81.35$ ;  $H=8.47$  per cent.).

It is very readily soluble in chloroform, ether, benzene, or acetone, less so in methyl alcohol or ethyl alcohol, and insoluble in water.

The rotatory-power determinations gave the following values without mutarotation:

Solvent.	Sub- stance. Gram.	Temper- ature.	$\alpha_D$ .	$[\alpha]_D$ .	$[M]_D$ .
Methyl alcohol .....	0.1678	$18^{\circ}$	$+1.32^{\circ}$	$+393.2^{\circ}$	$+1159.9^{\circ}$
Chloroform .....	0.1608	18	1.45	450.9	1330.0

*ar*-Tetrahydro- $\alpha$ -naphthylaminocamphor,



*ar*-Tetrahydro- $\alpha$ -naphthylaminocamphor crystallises from hot alcohol in reddish-brown needles melting at  $154$ – $155^{\circ}$  (Found:  $C=80.6$ ;  $H=8.7$ .  $C_{25}H_{25}ON$  requires  $C=80.8$ ;  $H=9.1$  per cent.).

It is very readily soluble in chloroform or ether, less readily so

in benzene or acetone, sparingly so in methyl alcohol or ethyl alcohol, and insoluble in water.

The rotatory-power determinations gave the following values without mutarotation:

Solvent.	Sub- stance. Gram.	Temper- ature.	$\alpha$ .	$[\alpha]_D$ .	$[M]_D$ .
Methyl alcohol .....	0.0548	20°	+0.12°	+109.5°	+325.2°
Chloroform .....	0.0809	20	0.19	117.1	347.8

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### CIX.—*Ortho-para-isomerism in the Preparation of Diaminodiphenylmethane.*

By HAROLD KING.

IN the course of an investigation of the nitro-derivatives of diaminodiphenylmethane, prepared either from dianilinomethane or from anhydroformaldehydeaniline and aniline, it was found that the crude, distilled diaminodiphenylmethane was a mixture of the 4:4'- and 2:4'-derivatives in the proportion of about 9 to 1. By crystallising the nitration products, 2:2'-dinitro-4:4'-diaminodiphenylmethane was first isolated, and from the mother liquors a mononitro-derivative, which, on removal of the amino-groups, subsequent reduction, and acetylation, gave 4-acetylamino-diphenylmethane. The mononitro-derivative must have arisen from 2:4'-diaminodiphenylmethane present in the starting material, as was confirmed by the separation of the two isomeric bases and the mono-nitration of the unsymmetrical base.

#### EXPERIMENTAL.

##### *Preparation of Diaminodiphenylmethane.*

*From Dianilinomethane.*—Fifty grams of crystalline dianilinomethane were digested with 59 c.c. of aniline, 31 c.c. of concentrated hydrochloric acid, and 24 c.c. of water for twelve hours at 95°. The product was made alkaline and completely freed from aniline by steam distillation. The residual non-volatile base, after washing by agitating with fresh quantities of water, was distilled

under reduced pressure, yielding 33 grams of crude diaminodiphenylmethane, which boiled at  $236\text{--}240^\circ/11\text{ mm.}$

*From Anhydroformaldehydeaniline.*—One hundred grams of solid anhydroformaldehydeaniline, 249 c.c. of aniline, 43 c.c. of water, and 130 c.c. of concentrated hydrochloric acid were mixed and heated on the water-bath for twelve hours. The crude, distilled aniline-free base boiled at  $238\text{--}242^\circ/15\text{ mm.}$ , and amounted to 148.5 grams.

*Nitration of Diaminodiphenylmethane and Isolation of  
4-Nitro-2:4'-diaminodiphenylmethane.*

Fifty grams of distilled diaminodiphenylmethane were nitrated by Benda's method (*Ber.*, 1912, 45, 1787). The crude nitration product was collected and extracted once when dry with a limited volume of boiling alcohol. The insoluble solid consisted of 2:2'-dinitro-4:4'-diaminodiphenylmethane, and amounted to 60.5 grams, which is 83 per cent. of the theoretical yield. As the material soluble in alcohol could not be purified by further crystallisation, the solution was evaporated to dryness, and the residual solid, amounting to 14.4 grams, dissolved in hot 10 per cent. hydrochloric acid solution and fractionally precipitated by addition of 10 per cent. solution of ammonia. After removal of tarry matter, further addition of ammonia to the hot solution caused the separation of a crystalline precipitate, and eventually a point was reached at which a turbidity developed, due to the incipient formation of an oil. The crystalline material was collected, and consisted of 6.3 grams of almost pure 2:2'-dinitro-4:4'-diaminodiphenylmethane. The filtrate was now completely precipitated with ammonia, and, when cold, the crude 4-nitro-2:4'-diaminodiphenylmethane (4.3 grams) was collected. The total yield of dinitro-base was about 92 per cent., and of the crude mononitro-base 7 per cent.

Another experiment, in which Ehrlich and Bauer's method (*Ber.*, 1915, 48, 502) of nitration was employed, furnished a 10 per cent. yield of crude mononitrodiaminodiphenylmethane.

4-Nitro-2:4'-diaminodiphenylmethane dissolves in about twenty-three parts of boiling alcohol, and crystallises in glistening, orange needles melting at  $157\text{--}158^\circ$  (corr.) (Found: C=64.4; H=5.5.  $\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_2$  requires C=64.2; H=5.4 per cent.).

The dihydrochloride crystallises in microscopic, hexagonal-shaped needles melting and decomposing at  $262^\circ$  (corr.) (Found: Cl=22.3.  $\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_2\cdot 2\text{HCl}$  requires Cl=22.4 per cent.).

The diacetyl derivative crystallises from acetic anhydride or

boiling methyl alcohol, in which it dissolves to the extent of 1.2 per cent. in pale buff-coloured, woolly needles melting at 239—240° (corr.) (Found: C=62.2; H=5.3.  $C_{17}H_{17}O_4N_3$  requires C=62.4; H=5.2 per cent.).

The *tetra-acetyl* derivative obtained when the diacetyl derivative is boiled with excess of acetic anhydride is soluble in about one hundred times its weight of boiling alcohol, and separates in clear, oblique prisms melting at 201.5—202.5° (corr.) (Found: C=61.6; H=5.4.  $C_{21}H_{21}O_6N_3$  requires C=61.3; H=5.1 per cent.).

*4:3'-Dinitro-2:4'-diacetylaminodiphenylmethane.*

4-Nitro-2:4'-diacetylaminodiphenylmethane (1.3 grams), when nitrated with a mixture of sulphuric and nitric acids, gave 1.45 grams of the crude dinitrated anilide. It was recrystallised twice from glacial acetic acid, yielding, finally, 1.15 grams. It dissolves in fifty volumes of the boiling solvent, and crystallises as a voluminous mass of golden needles melting at 264—265° (corr.). A mixture with the isomeric 3:3'-dinitro-4:4'-diacetylaminodiphenylmethane, which melts at 259—260° (uncorr.), melted at 233° (Found: C=55.3; H=4.4.  $C_{17}H_{16}O_6N_4$  requires C=54.3; H=4.3 per cent.).

*3':4-Dinitro-2:4'-diaminodiphenylmethane.*

The free aniline prepared from the above anilide, when recrystallised from boiling alcohol (twenty-four parts), separates in glistening, orange needles, very similar in appearance to 4-nitro-2:4'-diaminodiphenylmethane. It melts at 148.5—149.5° (corr.) (Found: C=54.5; H=4.2.  $C_{15}H_{12}O_4N_4$  requires C=54.2; H=4.2 per cent.).

*4-Acetylaminodiphenylmethane.*

4-Nitro-2:4'-diaminodiphenylmethane was deprived of the amino-groups by the diazo reaction, the product reduced, and acetylated. Purification by recrystallisation from alcohol gave the compound in the form of large, pearly leaflets melting at 128—129° (corr.), and a mixed melting point with 4-acetylaminodiphenylmethane, prepared from benzene and *p*-nitrobenzyl chloride by the Friedel and Crafts synthesis, followed by reduction and acetylation, showed no depression (Found: N=6.2.  $C_{15}H_{13}ON$  requires N=6.2 per cent.).

*Separation of 2:4'- and 4:4'-Diaminodiphenylmethanes.*

(a) *Use of Benzylidene Derivative.*—Crude, distilled diaminodiphenylmethane (148.5 grams) was converted into its dibenzylidene derivative. The alcoholic mother liquors were evaporated to dryness, and the residual semi-solid material was digested on the water-bath for two hours with 200 c.c. of 10 per cent. hydrochloric acid. The product was extracted with ether, and the acid aqueous solution rendered alkaline with ammonia and similarly extracted with ether. In this way, on removal of the solvent, 22.5 grams of syrup were obtained, which, on distillation under diminished pressure, gave 12 grams of a pale yellow oil. On acetylation, a crude diacetylamino-diphenylmethane was obtained, which was fractionally crystallised from alcohol. 9.5 Grams of pure 2:4'-diacetylamino-diphenylmethane were obtained, representing a minimum content of 4.5 per cent. of the ortho-para-base in the original material. The separation is difficult, and is only possible when the acetylated product contains excess of the ortho-para-isomeric.

(b) *Use of Differing Basicities.*—Seventy grams of crude, distilled diaminodiphenylmethane were dissolved in chloroform, and the solution was extracted thirty-two times by means of dilute sulphuric acid solution. Each extract contained 10 c.c. of 10 per cent. sulphuric acid solution diluted to such a volume as would keep the sparingly soluble sulphates in solution. In this way, solubility relationships were avoided, as attempts to separate the two bases by fractional crystallisation or precipitation of salts led to no result. The progress of the separation was followed by precipitating the acid fractions at intervals, by means of ammonia, and comparing the melting point of the acetyl derivatives with a mixed melting point with pure 4:4'-diacetylamino-diphenylmethane. By this means, it was found that the 2:4'-disubstituted base was concentrated in the last four extracts, which on acetylation gave 10.4 grams of solid material. This was fractionally crystallised from alcohol, when 5.0 grams of pure 2:4'-diacetylamino-diphenylmethane were obtained.

2:4'-Diacetylamino-diphenylmethane crystallises from boiling 95 per cent. alcohol (14 parts) in glistening, delicate, rectangular leaflets melting at 224—225° (corr.). It often melts at 209—210° (uncorr.), and if the molten contents are allowed to cool, it re-solidifies, and then re-melts at 224°. Occasionally the substance becomes semi-transparent at 210°, and then clears and forms a definite meniscus at 223—224°. Zincke and Prentzell (*Ber.*, 1905, 38, 4121), by recrystallisation from alcohol, obtained two modifications, white tablets melting at 208° and small needles melting



at 218°. The author has only once succeeded in reproducing the needle form, by inoculating a hot saturated solution of the anilide with the powdered, re-solidified material melting at 224°. Both forms separated simultaneously, the needle form in much the smaller proportion.

The identity of the 2:4'-diacetylaminodiphenylmethane was proved by direct comparison with a sample prepared by Staedel's method (*Annalen*, 1894, **283**, 162) from 2:4'-dinitrodiphenylmethane. Both showed the characteristic double melting point, and a mixture of the two showed no depression (Found: N=10.1. Calc.: N=10.1 per cent.).

2:4'-Diaminodiphenylmethane is readily soluble in hot benzene, but crystallises well from the cold solution in pearly leaflets. It melts at 88–89° (corr.) and boils at 222°/9 mm.

The dibenzylidene derivative is readily soluble in ether, and is precipitated on addition of light petroleum as an oil.

4:4'-Diaminodiphenylmethane, free from the isomeride, is best prepared through the intermediary of the dibenzylidene derivative. It crystallises well from benzene in clusters of rectangular plates melting at 92–93° (corr.) and boiling at 232°/9 mm.

#### 4:4'-Diamino-2:2'-azoxydiphenylmethane.

Pure 2:2'-dinitro-4:4'-diaminodiphenylmethane (1 gram) was suspended in 20 c.c. of alcohol, and 4 grams of crystalline, hydrated sodium sulphide, dissolved in 4 c.c. of water, were added. The solution was boiled for half an hour, and, when cold, the product, which separated in glistening, orange needles, was collected. The yield was 0.45 gram.

4:4'-Diamino-2:2'-azoxydiphenylmethane melts and decomposes at 265° (corr.) (Duval, *Compt. rend.*, 1905, **141**, 198, gives 272°). The only solvent at all suitable for its recrystallisation is pyridine (Found: C=64.9; H=5.3. Calc.: C=65.0; H=5.0 per cent.).

It forms a stable *dihydrochloride* crystallising in microscopic, six-sided leaflets, which are readily soluble in water without separation of the base. It has no definite melting point (Found: H<sub>2</sub>O=8.6; Cl=20.8. C<sub>13</sub>H<sub>12</sub>ON<sub>4</sub>·2HCl, 1½H<sub>2</sub>O requires H<sub>2</sub>O=7.9; Cl=20.8 per cent.).

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CX.—*Experiments on Halogenation. The Direct Displacement of Negative Groups by Halogen in the Aromatic Series. Part I. The Displacement of the Nitro-group by Bromine.*

By SURENDRA NATH DHAR.

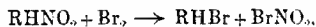
IN the series of which this paper is Part I, it is proposed to investigate the mechanism and conditions which lead to the direct displacement of negative groups by halogen atoms when such groups are attached to the aromatic nucleus, because, although several instances have been recorded of the occurrence of this type of reaction, no systematic study of it appears to have been made. It is evident that if a change of this kind could be definitely controlled and its course clearly established, it would serve as a valuable means for preparing certain aromatic derivatives not otherwise easily obtained.

In the first instance, therefore, it is intended to record certain experiments which have been carried out in connexion with the displacement of nitro-groups by bromine, a change which appears to have been first noted by Kekulé (*Annalen*, 1866, **137**, 169), when he obtained tri-, tetra-, and penta-bromobenzene by heating nitrobenzene with bromine in a sealed tube. Other instances of a similar character have since been published; thus, Meyer (*Monatsh.*, 1915, **86**, 723) found that nitrobenzene under the influence of thionyl chloride gives chlorobenzene, and that *m*-dinitrobenzene when treated with chlorine is converted first into *m*-chloronitrobenzene and finally into *m*-dichlorobenzene (D.R.-P. 108165). Picric acid gives with bromine the same bromodinitrophenol as is obtained when dinitrophenol is brominated (Armstrong, *J. Soc. Dyers*, 1885, **1**, 85). Other instances of the displacement of nitro-groups by halogens in the benzene as well as in the naphthalene series have been recorded by Lobry de Bruyn and Leent (*Rec. trav. chim.*, 1896, **15**, 84). Atterberg (*Ber.*, 1876, **9**, 316, 926, 1734; 1877, **10**, 1841), and Jolin (*Bull. Soc. chim.*, 1877, [ii], **28**, 514). Direct displacement of the nitro-group has also been noticed in the anthracene series. Thus 1-nitroanthraquinone is converted into 1-chloroanthraquinone through the agency of chlorine, and 1:5-dinitroanthraquinone into the 1:5-dichloro-derivative by the same process (D.R.-P. 252578).

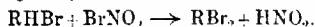
In the present paper are described experiments dealing with the behaviour of certain typical nitro-derivatives of benzene,

naphthalene, anthracene, xanthone, and coumarin towards bromine at a high temperature, when the bromine is present in the proportion of one molecule of the halogen to each nitro-group. These experiments were carried out with the object of settling one of the fundamental points in connexion with the reaction, namely, the reason why it does not stop when all the nitro-groups, or all such as are capable of displacement, are substituted by the halogen, but in many cases proceeds further, leading to the formation of higher halogenated derivatives. Moreover, preliminary experiments showed that not only did further halogenation take place with remarkable ease, but that it was possible by the aid of this reaction to prepare halogen derivatives which could not be obtained by the direct halogenation under known conditions. Examples of this kind are given in the experimental part, the best being that supplied by the formation of octabromoxanthone (p. 999).

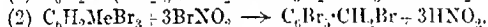
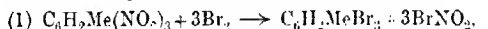
It is evident, therefore, that in this reaction some product is formed which acts as a very much more powerful halogenating agent than the halogen itself, and it is thought that this substance may well be the nitro-derivative of bromine, which might be formed in accordance with the equation



the reaction being completed in accordance with the equation



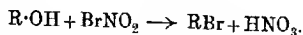
If this is the true explanation of the course of the reaction, it follows that a trinitro-derivative when treated with three molecules of bromine should, if a sufficient number of hydrogen atoms are present in the nitro-derivative, yield a compound containing six atoms of bromine, and that this is actually the case is shown by the behaviour of trinitrotoluene, which is transformed under these conditions into pentabromobenzyl bromide:



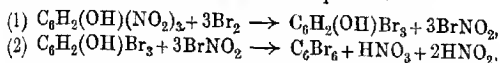
It may be added that this view is supported by the fact that in this and other similar cases the halogenation does not proceed further, even though excess of bromine is used. Similarly, both 1:5- and 1:8-dinitronaphthalene when treated with two molecular proportions of bromine yield the same tetrabromonaphthalene, which must therefore be the 1:(4):5:8-compound, the formation of the substance being in complete accord with the views expressed above.

It would be difficult to predict the reactions which might occur between the substance  $\text{BrNO}_2$  and phenols, but it is reasonable to suppose that one of them would be the displacement of the

hydroxyl by bromine and the formation of nitric acid, in accordance with the equation



It is therefore interesting to note that when picric acid is treated with three molecular proportions of bromine, it is converted into hexabromobenzene, although tetrabromo- and pentabromo-phenol are also produced. It is probable, therefore, that the reaction takes place chiefly in accordance with the equations



It is evident that both tetrabromo- and pentabromo-phenol are intermediate products in the reaction, because the yield of hexabromobenzene increases with the temperature of the reaction.

Although in the instances given above the displacement of the nitro-groups and subsequent bromination proceeds smoothly and completely, yet it is evident that the completion of the reaction must depend on two main factors, namely, (a) the stability of the nitro-group, and (b) the tendency for hydrogen atoms present in the molecule of the aromatic substance to be displaced by bromine. It is to be expected that experiment would reveal the operation of these two factors, and that instances would be found in which the reaction would leave nitro-groups in stable positions unattacked and in which the further entrance of bromine atoms would be inhibited. Actually, the experiments carried out with nitro-derivatives of xanthone and coumarin have supplied admirable examples of the operation of both factors, although in every case the course of the reaction can be explained by the general equations given above.

It may be added that all the nitro-compounds mentioned in this paper, excepting those of the coumarin series, have been treated with bromine in the usual solvents, such as acetic acid or nitrobenzene, without result. Compounds of the coumarin series do, however, yield bromo-derivatives under these conditions (see p. 1000). Thus both  $\alpha_1$ - and  $\beta_1$ -tetranitroxanthone give only dibromodinitroxanthone, and 3:6-dinitrocoumarin gives 3-bromo-6-nitrocoumarin when treated with four and two molecules of bromine respectively. On the other hand,  $\alpha_1$ -tetranitroxanthone gives tetrabromoxanthone, and 1:3- and 1:5-dinitroanthraquinone give 1:3- and 1:5-dibromoanthraquinone, respectively, under the same experimental conditions.

Further experiments, carried out under different conditions, will be necessary in order to determine the order in which the nitro-groups are displaced, and it is hoped that in this way valuable

evidence respecting the position-stability of this group will be forthcoming. Even in the present preliminary experiments, however, there is clear evidence of the remarkable stability conferred on nitro-groups occupying certain positions in an aromatic nucleus. It has been pointed out, for example, by Jordan and Thorpe (T., 1915, 107, 395) that whereas a nitro-group can be introduced into position 6 of the coumarin molecule with remarkable ease, it is a matter of considerable difficulty to introduce this group into position 3. The present experiments show that a nitro-group in position 6 cannot be displaced by bromine, and that one in position 3 is readily displaced. For example, 6-nitrocoumarin with one molecule of bromine yields 3-bromo-6-nitrocoumarin, and 3:6-dinitrocoumarin with two molecules of bromine gives the same 3-bromo-6-nitrocoumarin. Even when the last-named reaction is carried out at a high temperature, the nitro-group is not displaced, the final product being a tetrabromonitrocoumarin.

#### EXPERIMENTAL.

##### *Benzene Series. The Bromination of Picric Acid.*

Three grams of picric acid and 2 c.c. of bromine (3 mols.), together with a trace of iodine, were heated in a sealed tube at 220—250° for six hours. The crude product (4 grams), when treated with dilute alkali, yielded an insoluble residue which, when collected and recrystallised from benzene, was found to be hexabromobenzene, melting at 315° (Found: Br=86·87. Calc.: Br=86·96 per cent.). The precipitate obtained when the alkaline filtrate was acidified, when fractionally recrystallised from alcohol, yielded two substances. The less readily soluble one melted at 225°, and proved to be pentabromophenol (Found: Br=81·61.\* Calc.: Br=81·81 per cent.), and the more readily soluble one, which melted at 120°, was tetrabromophenol (Found: Br=78·53.\* Calc.: Br=78·03 per cent.).

The same products are obtained when the reaction is carried out at either 130° or at 300°, but the amount of hexabromobenzene formed is much greater at the higher temperature.

##### *The Bromination of 2:4:6-Trinitrotoluene.*

*Pentabromobenzyl Bromide.*—Three grams of 2:4:6-trinitrotoluene, 2 c.c. of bromine (3 mols.), and a trace of iodine were heated in a sealed tube at 200° for eight hours. The crude pro-

\* All halogen estimations were made by Robertson's method (T., 1915, 107, 902).

duct (2.5 grams), after being washed with dilute alkali, was crystallised from benzene, when it yielded slender, white needles melting at  $320^{\circ}$  (Found: Br=84.53.  $C_7H_2Br_5$  requires Br=84.80 per cent.). Pentabromobenzyl bromide is sparingly soluble in alcohol, and no precipitate of silver bromide is formed when its solution is treated with freshly precipitated silver hydroxide or alcoholic silver nitrate solution. It appears to be a remarkably stable substance, since it is not oxidised to pentabromobenzoic acid either by alkaline permanganate or by nitric acid in a sealed tube. It remains unchanged when heated in a sealed tube with bromine.

*Pentabromobenzyl Alcohol.*—This substance was obtained by heating a mixture of 1 gram of pentabromobenzyl bromide, 5 c.c. of absolute alcohol, and 2 grams of potassium acetate in a sealed tube at  $200^{\circ}$  for eight hours. It crystallises from alcohol in slender needles melting at  $175^{\circ}$  (Found: Br=79.82.  $C_7H_5OBr_5$  requires Br=79.52 per cent.). The compound is sparingly soluble in water, but dissolves readily in alcohol. It sublimes in colourless needles when heated at  $100^{\circ}$ .

*Naphthalene Series. The Bromination of 1:5- and of 1:8-Dinitronaphthalene.*

1:(4):5:8-Tetrabromonaphthalene.—Five grams of 1:5-dinitronaphthalene mixed with 2.5 c.c. of bromine (2 mols.) and a trace of iodine were heated in a sealed tube at  $200^{\circ}$  for five hours. The crude product (6 grams) crystallised from benzene in colourless needles melting at  $308^{\circ}$ , and the same compound is also obtained from 1:8-dinitronaphthalene under similar conditions (Found: Br=71.88.  $C_{10}H_4Br_4$  requires Br=72.06 per cent.).

1:(4):5:8-Tetrabromomononitronaphthalene was obtained by treating the above compound with concentrated sulphuric acid and nitric acid (D 1.42). For 1 gram of substance, 50 c.c. of each acid were used. A yellow precipitate was obtained on keeping the mixture overnight. The substance melts and decomposes at  $220^{\circ}$  (Found: N=2.83.  $C_{10}H_3O_2NBr_4$  requires N=2.86 per cent.).

*Hexabromonaphthalene.* This compound was prepared by heating 1.5 grams of 1:2:5:8-tetranitronaphthalene with 1 c.c. of bromine (4 mols.) and a trace of iodine in a sealed tube at  $220^{\circ}$  for twenty hours. The crude product (about 2 grams), after being washed with dilute aqueous alkali hydroxide, crystallised from benzene in white needles melting at  $280-285^{\circ}$  (Found: Br=79.60.  $C_{10}H_2Br_6$  requires Br=79.73 per cent.).

1:3:5:8-Tetrabromonaphthalene.—This substance was obtained by heating a mixture of 2 grams of 1:3:5:8-tetranitronaphthalene,

1.5 c.c. of bromine (4 mols.), and a trace of iodine in a sealed tube at 220° for twenty hours. The crude product (2.5 grams), after being washed with cold aqueous alkali hydroxide, crystallised from benzene in white needles melting at 310° (Found: Br=72.13.  $C_{10}H_4Br_4$  requires Br=72.06 per cent.).

1:3:5:8-Tetrabromonitronaphthalene.—Half a gram of the tetrabromo-compound was dissolved in 50 c.c. of concentrated sulphuric acid, 50 c.c. of nitric acid (D 1.42) were added, and the solution was heated over the steam-bath for one hour. When cold, a yellowish-brown precipitate was obtained by pouring the solution into water; this was collected and washed with water. The substance melts at 205° and does not decompose even at 280° (Found: N=2.76.  $C_{10}H_3O_2NBr_4$  requires N=2.86 per cent.).

1:2:6:8-Tetrabromonaphthalene.—This substance was obtained by heating 1.5 grams of 1:2:6:8-tetranitronaphthalene (p. 1004) with 1 c.c. of bromine (4 mols.) and a trace of iodine in a sealed tube at 220° for twenty hours. The substance was purified and crystallised, as in the case of hexabromonaphthalene, and obtained in yellowish-white, shining needles melting at above 315° (Found: Br=72.26.  $C_{10}H_4Br_4$  requires Br=72.06 per cent.).

1:2:6:8-Tetrabromonitronaphthalene was obtained by nitrating the above tetrabromo-compound, as in the case of the 1:3:5:8-tetrabromo-compound. A brownish-yellow substance was obtained which melted at 230° (Found: N=2.64.  $C_{10}H_3O_2NBr_4$  requires N=2.86 per cent.).

1:3:6:8-Tetrabromonaphthalene.—This was obtained by heating a mixture of 2 grams of 1:3:6:8-tetranitronaphthalene, 1.5 c.c. of bromine (4 mols.), and a trace of iodine in a sealed tube at 220° for twenty hours. White needles, melting at above 315°, were obtained by purifying the crude product (2 grams), as before (Found: Br=71.74.  $C_{10}H_4Br_4$  requires Br=72.06 per cent.).

1:3:6:8-Tetrabromonitronaphthalene was obtained as a brownish-yellow powder by nitrating the tetrabromo-compound, as in the previous cases. The substance melts at 210° (Found: N=2.77.  $C_{10}H_3O_2NBr_4$  requires N=2.86 per cent.).

#### *Xanthone Series. The Bromination of Tetranitroxanthones.*

In the following experiments a large excess of bromine was used, because preliminary experiments had shown that variation in the amount of halogen beyond the theoretical and in the temperature conditions did not affect the result.

*Dibromodinitroxanthone* was obtained by heating a mixture of

2 grams of  $\alpha_1$ -tetranitroxanthone,\* 3 c.c. of bromine (11 mols.), and a trace of iodine in a sealed tube at  $300^\circ$  for twenty-six hours. It crystallises from benzene (2 grams) in colourless needles melting at  $265^\circ$ . The same compound was obtained from  $\beta_1$ -tetranitroxanthone\* under similar conditions (Found: Br=36.22; N=6.16.  $C_{13}H_4O_6N_2Br_2$  requires Br=36.08; N=6.30 per cent.).

*Tetrabromoranthone*.—This substance (about 3 grams) was obtained by heating a mixture of 2.5 grams of  $\alpha_2$ -tetranitroxanthone,\* 4 c.c. of bromine (more than 11 mols.), and a trace of iodine in a sealed tube at  $300^\circ$  for twenty-six hours. It is isolated from its solution in benzene (in which it is very readily soluble) as an amorphous, yellow solid melting at  $255^\circ$  (Found: Br=62.36.  $C_{13}H_4O_6Br_4$  requires Br=62.50 per cent.). The compound is insoluble in alcohol and soluble in pyridine or acetic acid, but does not crystallise from either of these solvents. It is evidently different from the tetrabromoxanthone previously described (T., 1916, 109, 746), because it cannot be converted into a dinitro-derivative on nitration.

*Hexabromoranthone*.—This compound (about 4 grams) was prepared by heating 2.5 grams of  $\beta_2$ -tetranitroxanthone\* with 4 c.c. of bromine (more than 11 mols.) and a trace of iodine in a sealed tube at  $200^\circ$  for thirty hours. It crystallises from benzene in slender, yellow needles melting at  $288^\circ$  (Found: Br=72.01.  $C_{13}H_2O_6Br_6$  requires Br=71.63 per cent.). This compound is evidently different from that previously described (T., 1916, 109, 748), because it does not yield a colouring matter when heated with aniline and a trace of copper powder.

*Octabromoranthone*.—One gram of tetrabromodinitroxanthone (*loc. cit.*), 3 c.c. of bromine (36 mols.), and a trace of iodine were heated in a sealed tube at  $300^\circ$  for thirty-six hours. The product crystallised from benzene in slender, colourless needles melting at above  $315^\circ$  (Found: Br=77.57.  $C_{13}O_2Br_8$  requires Br=77.31 per cent.).

#### Anthraquinone Series.

1:3-Dibromoanthraquinone was obtained by heating 2.2 grams of 1:3-dinitroanthraquinone, 1 c.c. of bromine (2 mols.), and a trace of iodine in a sealed tube at  $200$ – $250^\circ$  for seven hours, and at  $290^\circ$  for a further hour. It crystallises from alcohol in canary-yellow needles melting at  $210^\circ$ , as stated by Ullmann and Eiser (*Ber.*, 1916, 49, 2154) (Found: Br 44.16. Calc.: Br=43.71 per cent.).

\* The new tetranitroxanthones mentioned in this paper will be described in a later communication.



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1:5-Dibromoanthraquinone was obtained by heating 5 grams of 1:5-dinitroanthraquinone, 2 c.c. of bromine (2 mols.), and a trace of iodine in a sealed tube at 300° for four hours. The substance crystallises from benzene in pale yellow needles melting at above 320° (Found: Br=43·48. Calc.: Br=43·71 per cent.).

### *Coumarin Series.*

3-Bromo-6-nitrocoumarin.—Three grams of 6-nitrocoumarin were heated with 2 c.c. of bromine (3 mols.) and a trace of iodine in a sealed tube at 130° for eight hours. The crude product (3·5 grams), after being washed with water, crystallised from alcohol in colourless needles melting at 215° (Found: Br=29·96; N=5·26. Calc.: Br=29·63; N=5·18 per cent.).

This compound is also obtained when 3:6-dinitrocoumarin is treated in a similar manner, or when 6-nitrocoumarin is heated in an open tube with bromine in acetic acid solution.

3:8-Dibromo-6-nitrocoumarin.—This substance was prepared by heating a solution of 4·5 grams of 3:6-dinitrocoumarin in 10 c.c. of acetic acid with 4 c.c. of bromine and a trace of iodine on a sand-bath for twenty hours. The product, after being washed with alcohol, crystallised from benzene in white needles melting at 220° (Found: Br=45·89; N=4·19.  $C_9H_5O_4NBr_2$  requires Br=45·84; N=4·01 per cent.).

3:8:1-Tribromo-6-nitrocoumarin.—This compound was prepared by heating a mixture of 3 grams of 3:6-dinitrocoumarin, 2 c.c. of bromine (3 mols.), and a trace of iodine in a sealed tube at 180° for six hours. The crude product was purified by solution in cold aqueous alkali hydroxide, precipitation by dilute hydrochloric acid, and crystallisation from alcohol; it melts at 200—205° (Found: Br=56·46; N=2·77.  $C_9H_3O_4NBr_3$  requires Br=56·08; N=3·26 per cent.). In this reaction a second product was formed which was insoluble in alkali hydroxide, and proved to be tetrabromonitrocoumarin (see below).

3-Bromo-6:8-dinitrocoumarin was obtained by heating 1·5 grams of 3:6:8-trinitrocoumarin dissolved in 5 c.c. of acetic acid with 2 c.c. of bromine and a trace of iodine on a sand-bath for twenty hours. The crude product, after being washed with cold aqueous alkali hydroxide, separated from alcohol as a yellowish-white solid melting at 130—135° (Found: Br=25·82; N=8·48.  $C_9H_3O_6N_2Br$  requires Br=25·40; N=8·87 per cent.).

3:8:1:1-Tetrabromo-6-nitrocoumarin.—A mixture of 1·5 grams of 3:6:8-trinitrocoumarin with 1 c.c. of bromine (4 mols.) and a trace of iodine was heated in a sealed tube at 160° for six hours.

After being washed with dilute alkali, the product crystallised from alcohol in pale yellow needles melting at  $260^{\circ}$  (Found: Br=63.29; N=2.58.  $C_9H_5O_4NBr_4$  requires Br=63.10; N=2.79 per cent.).

The author wishes to express his thanks to Professor J. F. Thorpe and to Dr. M. A. Whiteley for their kind encouragement during the course of the work, and to the Research Fund Committee of the Chemical Society for a grant which has defrayed the cost of some of the materials.

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### CXI.—Some Nitro-derivatives of Naphthalene and Anthraquinone.

By SURENDR NATH DHAR.

THE present study was undertaken mainly with the view of preparing some nitro-compounds for halogenation in the manner dealt with in the previous paper. One remarkable fact has, however, been brought to light in connexion with the nitration of anthraquinone.

It is well known that when anthraquinone is nitrated, a mixture of dinitroanthraquinones is formed, and from such a mixture the nitro-compounds can be separated only with very great difficulty, using solvents such as acetone, pyridine, etc. By this method, only the following dinitroanthraquinones have been isolated from different mixtures: 1:5-, 1:6-, 1:7-, 1:8-, 2:6-, and 2:7- (D.R.-P. 167699).

It will be seen that, of the ten possible dinitro-compounds, the 1:2-, 1:3-, 1:4-, and 2:3-derivatives are missing. It is natural to suspect that some of these four isomerides might be left undetected in the mixtures, because of the unsatisfactory method of separation. It was therefore thought that the new method of bromination might help in detecting the unknown dinitro-compounds, if any. This expectation has been fulfilled.

A mixture of dinitroanthraquinones, obtained by nitrating anthraquinone by the ordinary method, was treated with bromine in a sealed tube, and the product was found to be a mixture of

1:2- (m. p. 268°), 1:3- (m. p. 210°), 1:5- (m. p. above 360°), and 2:6- (m. p. 285°) dibromoanthraquinones.

Attempts were then made to isolate the corresponding four dinitro-compounds. As a result of nitration under different conditions with different proportions of nitric and sulphuric acids, four dinitro-compounds have actually been obtained, but only two of them have been identified, and characterised as 1:5- and 1:3-dinitroanthraquinones respectively.

By the nitration of 1:8-dinitronaphthalene, Will (*Ber.*, 1895, 28, 378) obtained only one of the two possible tetranitronaphthalenes, and characterised it as the 1:3:6:8-tetranitro-derivative; but in the present work both the tetranitro-compounds have been isolated, so that the new compound is necessarily 1:2:6:8-tetranitronaphthalene. Two trinitro- $\beta$ -naphthoic acids have been obtained by the nitration of  $\beta$ -naphthoic acid.

It may here be stated that nitric acid has been found to be a useful solvent for nitro-compounds in general. By using this, not only are costly solvents avoided, but the separation of different nitro-compounds and their purification are accomplished with very great ease.

#### EXPERIMENTAL.

##### *Anthraquinone Series.*

Ten grams of anthraquinone were added gradually to a mixture of 250 grams of concentrated sulphuric acid and 250 grams of nitric acid (D 1.42) with shaking. The solution was kept over the steam-bath for about an hour, when yellow needles were obtained, which were collected over asbestos. The substance melted at 312—317°, and was found to be a mixture of dinitro-compounds. It was heated with two molecular proportions of bromine and a trace of iodine in a sealed tube for six hours between 250° and 300°. From the product, four different dibromoanthraquinones were separated by means of laborious fractional crystallisation. The crude product yielded an insoluble residue when boiled with alcohol. From the alcoholic solution two substances separated on fractional crystallisation. The less soluble one melted at 268° and proved to be 1:2-dibromoanthraquinone (Found: Br=44.21. Calc.: Br=43.71 per cent.), and the more readily soluble one, which melted at 210°, to be 1:3-dibromoanthraquinone (Found: Br=43.96). The insoluble residue yielded two other substances when fractionally crystallised from benzene. The more readily soluble one melted at 285°, and was 2:6-dibromoanthraquinone (Found: Br=43.98), and the less soluble one, which did

not melt up to  $360^{\circ}$ , was 1:5-dibromoanthraquinone (Found: Br=44.87).

Twenty-five grams of anthraquinone (sublimed) were mixed with concentrated sulphuric acid in a mortar, and the mixture was washed with sulphuric acid into a large flask. A further quantity of sulphuric acid was added to make the total amount of acid 300 c.c., and 400 c.c. of nitric acid were then added to the mixture. The flask was kept over the steam-bath for six hours, when yellow crystals precipitated. These were filtered over asbestos and washed with nitric acid and then with water. The substance was further purified by boiling with nitric acid. It did not melt up to  $360^{\circ}$ , and was identified as 1:5-dinitroanthraquinone (Found: N=9.31. Calc.: N=9.39 per cent.).

When boiled with sodium methoxide, it gave a dimethoxy-compound which melted at  $236^{\circ}$  (1:5-dimethoxyanthraquinone melts at  $236^{\circ}$  (D.R.-P. 167699), and when heated in a sealed tube with bromine and iodine a dibromo-compound was obtained which did not melt up to  $300^{\circ}$ .

*1:3-Dinitroanthraquinone.*—From the filtrate and washings of 1:5-dinitroanthraquinone another dinitro-compound was obtained by precipitation with water. It crystallised from nitric acid in yellow needles (5 grams) melting at  $240^{\circ}$  (Found: N=4.2.  $C_{14}H_6O_6N_2$  requires N=9.39 per cent.).

When boiled with sodium methoxide it gave 1:3-dimethoxyanthraquinone melting at  $155^{\circ}$  (Graebe, *Annalen*, 1906, **349**, 230, gives  $150-153^{\circ}$ ).

*3-Nitro-1-aminoanthraquinone.*—1:3-Dinitroanthraquinone was reduced with alcoholic ammonium sulphide in the usual way. For each gram of the nitro-compound, 50 to 75 c.c. of alcohol and 20 to 25 c.c. of ammonia were required. The nitroamino-compound crystallised from alcohol in deep red needles which melted at  $265^{\circ}$  (Found: N=10.48.  $C_{14}H_8O_4N_2$  requires N=10.45 per cent.).

*3-Nitroanthraquinone-1- $\alpha$ - $\beta$  naphthol.*—The nitroamino-compound was diazotised in the usual way and combined with  $\beta$ -naphthol. The product separated from alcohol as a deep red, amorphous substance melting at  $235-240^{\circ}$  (Found: N=9.98.  $C_{21}H_{13}O_5N_3$  requires N=9.92 per cent.).

3-Nitro-1-hydroxyanthraquinone was obtained by diazotising the nitro-amino-compound and warming the solution over the steam-bath for ten hours. It separated as a brick red, amorphous powder melting at  $240^{\circ}$  (R. Scholl, *Ber.*, 1904, **37**, 4435, gives  $247-248^{\circ}$ ) (Found: N=5.01. Calc.: N=5.20 per cent.).

Very small amounts of two other dinitro-compounds were

obtained from the nitric acid filtrates from 1:5- and 1:3-dinitro-anthraquinones, and they are under investigation.

Nitration of both 1:5- and 1:3-dinitroanthraquinone was tried with mixtures of sulphuric and fuming nitric acids in various proportions by boiling over a sand-bath under reflux, but in each case the substance decomposed completely.

#### *Naphthalene Series.*

1:2:6:8-Tetranitronaphthalene.—Five grams of 1:8-dinitronaphthalene were dissolved in a mixture of 25 c.c. of concentrated sulphuric acid and 25 c.c. of nitric acid (D 1.5). The solution was kept over the steam-bath for about four hours, when about 2 grams of a white powder were obtained. The substance does not melt up to 300° (Found: N=18.20.  $C_{10}H_4O_8N_2$  requires N=18.18 per cent.).

From the filtrate about 2 grams of 1:3:6:8-tetranitronaphthalene were obtained, which was purified by crystallisation from nitric acid.

Trinitro- $\beta$ -naphthoic Acid.—Two grams of  $\beta$ -naphthoic acid were dissolved in 40 c.c. of concentrated sulphuric acid, and 25 c.c. of nitric acid (D 1.42) were added to the solution. On keeping the solution overnight, needles melting at 220° separated (Found: N=13.58.  $C_{11}H_5O_8N_3$  requires N=13.68 per cent.).

From the filtrate another trinitro-compound, much in excess of the first, was obtained as a yellow precipitate on the addition of water. It melted and decomposed at 215° (Found: N=13.47.  $C_{11}H_5O_8N_3$  requires N=13.68 per cent.).

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## CXII.—*The Action of the Grignard Reagent on Aromatic Nitro-compounds.*

By HARRY HEPWORTH.

THE reaction between nitro-compounds and the Grignard reagent does not appear to have been the subject of many investigations. The earliest communication is that of Moureu (*Compt. rend.*, 1901, **132**, 837), who obtained  $\beta\beta$ -diethylhydroxylamine by the action of magnesium ethyl iodide on amyl nitrite and nitroethane,

and a product, which was probably  $\beta\beta$ -dimethylhydroxylamine, by the action of magnesium methyl iodide on methyl nitrate.

Iocitsch (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 555) studied the action of magnesium phenylacetylene bromide on nitrobenzene in ethereal solution, and found that a crystalline compound was formed which, when decomposed with water, yielded a hydrocarbon,  $C_{10}H_{10}$  (m. p.  $87-88.5^\circ$ ). The constitution of this hydrocarbon was not further investigated.

Oddo (*Atti R. Accad. Lincei*, 1904, [v], **13**, ii, 220) was the first to study the action of the Grignard reagent on any aromatic nitro-compounds in detail. His investigation was confined to a study of the action of magnesium ethyl iodide on nitrobenzene. It was found that when this was cautiously added to a well-cooled ethereal solution of magnesium ethyl iodide, a yellow compound,  $O,NPhEt \cdot O \cdot MgI$ , was precipitated, but on the addition of a further quantity of nitrobenzene, the precipitate suddenly became dark brown. The yellow compound gave with pyridine an additive compound,  $C_8H_{10}O_2NMgI, C_4H_5N$ , and also, when decomposed with water, gave rise to ethylaniline and a product, which Oddo describes as a red, uncrystallisable oil, with an odour suggestive of almonds. Beyond the separation of this oil into three fractions, it was not further investigated.

Bewad (*Ber.*, 1907, **40**, 3065) studied the action of magnesium or zinc alkyl iodides on esters of nitrous acid and on nitro-paraffins. It was found that in the preparation of  $\beta$ -dialkylhydroxylamines, the zinc alkyl usually employed can be replaced advantageously by zinc alkyl iodides or magnesium alkyl iodides when the esters of nitrous acid are used, but not in the case of nitro-paraffins. With the latter, the reaction follows two courses, in both cases the final product being a  $\beta$ -dialkylhydroxylamine, the one containing one alkyl group derived from the magnesium alkyl haloid employed, the other containing two.

In a short note (*P.*, 1907, **23**, 153), Pickard and Kenyon described the results of some preliminary experiments on the action of *p*-nitrotoluene on magnesium alkyl haloids in ethereal solution. It is stated that *p*-nitrotoluene reacts very vigorously with organo-magnesium haloids in ethereal solution, thus forming an indefinite, amorphous, yellow compound, which, when treated with acids, yields principally *p*-nitrosotoluene, *p*-tolylhydroxylamine, 4:4'-azoxytoluene (probably by the interaction of the two former compounds), and *p*-toluidine.

It will thus be seen that comparatively little work has been carried out on the behaviour of the Grignard reagent with nitro-compounds, and it was decided to investigate the action of mag-

nesium methyl iodide and magnesium ethyl bromide on the simple mononitro-aromatic compounds, nitrobenzene, *o*- and *p*-nitrotoluenes, and  $\alpha$ -nitronaphthalene. In these experiments, the Grignard compound was not prepared separately, but a mixture of nitro-compound and alkyl haloid, diluted with ether, was added drop by drop to well-cooled ether containing magnesium powder, the rate of addition of magnesium powder being such as to keep the magnesium in excess throughout the reaction. This method was first employed by Kipping and Davies (T., 1911, **99**, 296), and has been found by the author to be convenient in certain reactions where selective action of the Grignard compound is aimed at (T., 1919, **115**, 1203).

In this way, it was found that the rate of reaction between the nitro-compounds and the Grignard reagents could be controlled fairly easily, provided that the flask in which the reaction is carried out is cooled in ice.

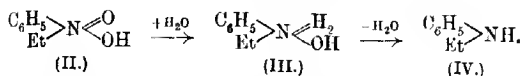
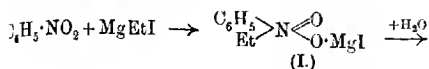
With nitrobenzene and magnesium methyl iodide or magnesium ethyl bromide, the existence of compounds corresponding with Oddo's compound,  $\text{O:NPhEt}\cdot\text{O}\cdot\text{MgI}$  (*loc. cit.*), has been confirmed. These compounds are pale yellow, and are best formed when the ratio of nitro-compound to magnesium alkyl haloid is about 2:3. On keeping for a few hours, these compounds become dark brown, especially if the temperature is allowed to rise. On decomposing the yellow additive compound with water, ethylaniline and azobenzene, together with unchanged nitrobenzene, were found to be the principal products of reaction. Magnesium methyl iodide reacted rather more energetically with nitrobenzene, with the production of methylaniline and azobenzene.

In a similar manner, it was found that magnesium ethyl bromide reacted with *p*-nitrotoluene, with the production of ethyl-*p*-toluidine and 4:4'-azotoluene, whilst magnesium methyl iodide gave rise to methyl-*p*-toluidine and 4:4'-azotoluene. With *o*-nitrotoluene, the analogous *o*-derivatives were formed. Under the conditions of the experiments, the formation of nitroso-compounds, hydroxylamine derivatives, and azoxy-compounds was not observed.

Finally, a few experiments were carried out with  $\alpha$ -nitronaphthalene, from which moderate quantities of methyl- and ethyl- $\alpha$ -naphthylamines were obtained, whilst small quantities of  $\alpha\alpha'$ -azonaphthalene were also isolated.

Oddo (*loc. cit.*) has already suggested a possible mode of reaction to account for the formation of ethylaniline from nitrobenzene, and a similar view may be propounded to account for the production of bases from the other compounds studied by the

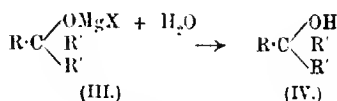
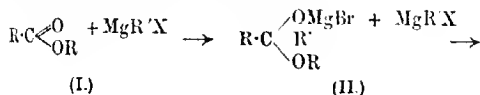
present author. According to Oddo, the primary reaction may be written as follows:



The experimental evidence which Oddo brings forward, and has now been confirmed, certainly justifies the formulation of compound I, but the formation of ethylaniline (IV) by the intermediate formation of III is open to question. There seems to be no objection to postulating that compound II loses oxygen directly with the formation of ethylaniline (IV). No compound analogous to II is known, so that it is impossible to speak with any degree of certainty as to its behaviour. At the same time, the loss of oxygen from such a compound is no more remarkable than the loss of carbon dioxide in the conversion of a simple monocarboxylic acid into the corresponding hydrocarbon, the more so if one accepts, what is probably the case, that compound II is very unstable and just as likely to lose oxygen as compound III is to lose water. In either case, compound II must lose oxygen prior to its conversion into ethylaniline.

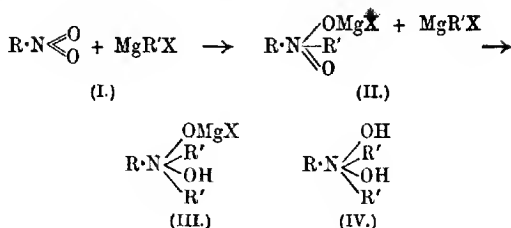
The production of the other secondary bases may be accounted for in an analogous manner.

It is now necessary to account for the formation of azo-compounds without postulating the formation of nitroso-compounds or hydroxylamine derivatives during the course of the reaction. In this connexion, it is interesting to compare the action of excess of Grignard reagent with the esters of the simpler carboxylic acids and with the aromatic nitro-compounds. In the former case, the course of the reaction is as follows:



In the case of the aromatic nitro-compounds, the reaction may be represented as follows:





Two molecules of III may be condensed, with the primary production of one molecule of an azo-compound and four molecules of  $\text{Mg}(\text{OR})\text{Br}$ , or, on the addition of water, a compound of the type IV may be momentarily formed, two molecules of which lose four molecules of alcohol to give an azo-compound. At the same time, the intermediate formation of a compound such as the latter would be expected to give rise eventually to a dialkylaniline oxide.

In this connexion, it is interesting to note that azobenzene has also been prepared by Wieland and Roseau (*Ber.*, 1912, **48**, 494) by the action of excess of magnesium phenyl bromide on nitrosobenzene, for which no explanation as to the mechanism of the reaction is given.

#### EXPERIMENTAL.

About 2 grams of magnesium powder and 5 grams of ethyl bromide, together with 200 c.c. of dry ether, were placed in a large flask provided with a stirrer, a reflux condenser, and a small, wide glass tube for the introduction of magnesium, and the reaction was started by introducing a little magnesium ethyl bromide prepared in a test-tube.

When the reaction was proceeding satisfactorily, the flask was surrounded by a mixture of ice and salt, and 123 grams (1 mol.) of freshly distilled nitrobenzene, 170 grams of ethyl bromide ( $1\frac{1}{2}$  mols.), and 300 c.c. of dry ether were now added drop by drop to the well-stirred mixture, the whole addition taking about four and a-half hours. Forty grams ( $1\frac{1}{2}$  mols.) of magnesium powder were introduced a little at a time in such a way as to ensure the presence of excess of magnesium throughout the reaction. The addition of each drop of the ethereal solution of ethyl bromide and nitrobenzene produced a hissing sound and a yellow precipitate. Towards the end of the addition the reaction became less vigorous.

A small quantity of the yellow precipitate was withdrawn, filtered, and quickly freed from any adhering magnesium powder.

After washing with a little ice-cold ether, a portion of the precipitate was converted into the pyridine double compound by boiling with pyridine under reflux for six hours, as described by Oddo (*loc. cit.*) (Found: Mg=7.31; N=8.30. Calc.: Mg=7.27; N=8.36 per cent.).

After remaining overnight, the contents of the flask had become dark brown. Sufficient water was added drop by drop to the well-cooled mixture, and the reaction vessel was warmed in order to remove a large portion of the product, which had adhered firmly to the walls.

The product was then extracted six to seven times with ether, the clear separation of the ethereal layer being accelerated in a centrifuge. The aqueous portion did not then contain more than traces of organic matter. After drying the ethereal layer, the ether was evaporated to 200 c.c., and then thoroughly extracted several times with aqueous oxalic acid in order to remove the bases present.

*Ethereal Solution Free from Base.*—The ethereal solution was dried, and, after removal of the ether, distilled under 15 mm. pressure. Six fractions were collected, as follows:

I. 115—123°, 22 grams	IV. 146—165°, 14 grams
II. 123—130°, 14 "	V. 168—175°, 7 "
III. 130—144°, 8 "	VI. 175—195°, 12 "

Above 195°, decomposition occurred, and the distillation was stopped. The residue in the flask weighed 8 grams. All these fractions were red. Fractions IV, V, and VI readily solidified in ice, whilst fraction III solidified on keeping in ice for twenty-four hours. These were transferred to a porous plate, and a red solid (m. p. 61—64°) was obtained. On recrystallisation from 90 per cent. alcohol, 27 grams of a substance crystallising in large red plates (m. p. 68.5°) were obtained. The identity of this product with azobenzene was established by its conversion into hydrazobenzene and benzidine. Thirty-four grams of unchanged nitrobenzene (b. p. 207°) were recovered on refractionating fractions I and II.

*Oxalic Acid Extract.*—Preliminary experiments had indicated that no hydroxylamine derivative was present in the acid extract. As this solution appeared to contain traces of impurities not extractable by ether, it was distilled in a current of steam for one hour. Traces only of a brownish-red oil passed over. The residue was rendered alkaline and the steam distillation continued until no more oil passed over. The oil was extracted with ether, dried, and, after removal of the ether, dried in a vacuum over solid

potassium hydroxide and paraffin wax. Twenty-five grams of an oil with an odour like that of aniline and a faint brown colour were obtained.

This oil distilled at 205—208°/762 mm., and was identified as ethylaniline. A sample submitted to analysis by the *R*-salt and acetic anhydride method did not show more than traces of primary or tertiary bases. A freshly distilled sample (b. p. 206—206.5°) was converted into the platinichloride (Found: Pt=30.0. Calc.: Pt=29.9 per cent.).

*Action of Magnesium Methyl Iodide on Nitrobenzene.*

This was carried out on similar lines to the previous experiment, 62 grams of nitrobenzene, 106 grams (1½ mols.) of methyl iodide, and 19 grams (1½ mols.) of magnesium powder being employed. The reaction was rather more vigorous, and yielded 22 grams of unchanged nitrobenzene, 15 grams of methylaniline, and 17 grams of azobenzene. In a further experiment, an attempt was made to separate the azobenzene and methylaniline from the dark product, obtained on decomposing the Grignard compound with water, by distillation in a current of steam. This was found to be extremely slow, and even after twelve hours' continuous distillation azobenzene continued to pass over. In subsequent experiments, the original method of separating the base by means of aqueous oxalic acid was reverted to, the residue being thoroughly dried and then distilled in a vacuum. The identity of the base with methylaniline was established by analysis of the platinichloride (Found: Pt=31.10. Calc.: Pt=31.24 per cent.).

*Action of Magnesium Ethyl Bromide and Magnesium Methyl Iodide on p-Nitrotoluene.*

A mixture of 40 grams of *p*-nitrotoluene, 70 grams (2 mols.) of ethyl bromide, and 150 c.c. of dry ether was added during three hours to 16 grams (2 mols.) of magnesium powder and 200 c.c. of ether, as in the previous experiments. At first a yellow precipitate was formed, but this was very transient, and the mixture quickly became brown.

The base was separated as before. On rendering alkaline and continuing distillation, a base (b. p. 216—219°) was collected. On redistillation, 9 grams of an oil (b. p. 216—217°) were obtained, which was identified as ethyl *p*-toluidine (Found: N=10.56. Calc.: N=10.4 per cent. In platinichloride: Found: Pt=29.0. Calc.: Pt=28.7 per cent.).

The residue left from the extraction of the base was dried and distilled under 20 mm. pressure.

Three fractions were obtained.

Fraction 1,	110—135°,	5 grams
"	2, 140—160°,	5 "
"	3, 185—200°,	16 "

On working up fractions 2 and 3 as before, 17 grams of crude 4:4'-azotoluene were obtained, which, on recrystallisation from alcohol containing a little light petroleum, separated in long, yellow needles melting at 143·6° (Found: N=13·28. Calc.: N=13·37 per cent.). A mixture with an equal quantity of pure 4:4'-azotoluene melted at 144°.

In a similar experiment, in which 93 grams of methyl iodide were used in place of 72 grams of ethyl bromide, 8 grams of methyl-*p*-toluidine (b. p. 208—209°) and 15 grams of 4:4'-azotoluene (m. p. 144°) were obtained.

The effect of increasing the amount of alkyl haloid and magnesium was investigated, the quantity being raised to four molecular proportions to one of *p*-nitrotoluene. It was found that rather more azo-compound and base were produced, but even in these experiments there was some unchanged *p*-nitrotoluene.

#### *Action of Magnesium Ethyl Bromide and Magnesium Methyl Iodide on o-Nitrotoluene.*

A mixture of 40 grams of *o*-nitrotoluene, 72 grams of ethyl bromide, and 16·5 grams of magnesium powder was allowed to react exactly as in the case of *p*-nitrotoluene when 8 grams of ethyl-*o*-toluidine (b. p. 204—206°) and 12 grams of 2:2'-azotoluene (m. p. 55·4°) were obtained.

In a similar experiment, using 40 grams of *o*-nitrotoluene, 95 grams of methyl iodide and 16·5 grams of magnesium powder, 9 grams of methyl-*o*-toluidine (b. p. 207—208°) and 11 grams of 2:2'-azotoluene were obtained.

#### *Action of Magnesium Ethyl Bromide and Magnesium Methyl Iodide on α-Nitronaphthalene.*

A mixture of 52 grams of α-nitronaphthalene, 50 grams of ethyl bromide, and 200 c.c. of dry ether was slowly added to 200 c.c. of dry ether, to which 11 grams of magnesium powder were added in small portions from time to time. The usual yellow precipitate was formed, which became brown on keeping overnight. After decomposition with water, a base was extracted with oxalic acid, as in the previous experiments.

On rendering the acid extract alkaline and distilling in a current of steam, 15 grams of an oily base (b. p. 298—301°/754 mm.) were obtained. On keeping, the base became much darker, and appeared brown by transmitted light and violet-blue by reflected light. It was further purified by dissolving in dry ether and precipitating the hydrochloride with dry hydrogen chloride. The base, liberated by aqueous potassium hydroxide, boiled at 187—189°/15 mm. The platinichloride was analysed (Found: Pt=25·80. Calc.: Pt=25·93 per cent.).

This base therefore appears to be ethyl- $\alpha$ -naphthylamine, and its liberation from its salts by means of alkalis confirms the experiments of Morgan and Micklethwait (T., 1907, 91, 1516), who negatived the statement of Limpriht (*Annalen*, 1856, 99, 117) and Schiff (*ibid.*, 1857, 101, 90) that the salts of this base, on treatment with potassium hydroxide, yielded  $\alpha$ -naphthylamine.

The residue, after removal of the base, could not be distilled without decomposition, even under diminished pressure. The separation of a little  $\alpha\alpha'$ -azonaphthalene was achieved by precipitating an ethereal solution of the residue with dry hydrogen chloride. This precipitation was repeated several times, when a dark brown solid was eventually obtained. From this material 3 grams of  $\alpha\alpha'$ -azonaphthalene were obtained by careful sublimation. The sublimate was obtained as yellow leaflets which, on rubbing, became yellowish-red. On recrystallising from acetic acid, the substance was obtained in green needles melting at 185—189° (Found: N=10·10. Calc.: N=9·96 per cent.).

One gram of this substance was converted into hydrazonaphthalene by treating with 1·5 grams of solid sodium hydroxide and 100 c.c. of alcohol, heating to boiling, and adding zinc dust until colourless. On filtering into dilute yellow ammonium sulphide solution, separating, drying, and recrystallising from benzene, a substance was obtained which, when mixed with hydrazonaphthalene, melted at 275—276°.

A similar experiment with methyl iodide gave 16 grams of methyl- $\alpha$ -naphthylamine (b. p. 293—295°) and a small yield of  $\alpha\alpha'$ -azonaphthalene.

The author is indebted to the Research Committee of Messrs. Nobel's Explosives Company, Limited, and particularly to Mr. Rintoul, for the facilities accorded him in carrying out this investigation.

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## Organic Chemistry.

**Polymerisation.** H. STAUDINGER (*Ber.*, 1920, 53, [B], 1073—1085).—During recent years there has been a noticeable tendency to formulate polymerisation products as molecular compounds in which the individual portions are united by means of partial valencies. In the author's opinion, this tendency is to be deprecated, since, in the present state of our knowledge, such compounds can be represented by normal valency formulae.

Polymerisation processes are defined as those in which two or more molecules unite to form a product of the same composition, but greater molecular weight. Two types of product are to be distinguished: (1) "true" polymerisation products, in which the atoms are united in the same manner as in the unimolecular compound (hexaphenylethane from triphenylmethyl, paraldehyde from acetaldehyde, etc.), and (2) "condensed" polymerisation products, in which a more or less atomic displacement has occurred (aldol polymerisation, benzoin formation, etc.). The first case only is discussed in the present communication. Polymerisation occurs with substances containing an unsaturated atom, or, more generally, with those which have an unsaturated linking, in which case rings containing 4, 6, or 8 atoms are formed, or else a product of very high molecular weight. It appears impossible at present to predict the direction in which action will take place. On the other hand, more general information is available on the stability of polymerides and their tendency towards depolymerisation. 4-Atom rings are generally less stable than those with 6 atoms, as is to be expected from Baeyer's strain theory. Heterocyclic four-membered rings are usually less stable than *cyclobutane* derivatives. The permanence of the latter, however, is greatly modified by substitution, and can be greatly weakened by the introduction of phenyl or carbonyl groups. The six-membered rings, particularly those which are *isocyclic*, are relatively stable, though fission occurs more frequently with heterocyclic systems. The possibility of smooth depolymerisation to the unimolecular substance depends, not only on the temperature of decomposition of the polymeride, but also on the stability of the simpler compound.

In the light of these general considerations, the literature of the formation of four-, six-, and eight-membered rings is critically reviewed, and it is shown that all known stable polymerisation products can be expressed by formulae with normal valencies. For the highly complex products, such as paraformaldehyde, the

formula  $\begin{matrix} \text{H}_2 & \text{H}_2 & & \text{H}_2 & \text{H}_2 \\ & | & & | & | \\ \text{C} \cdot \text{O} \cdot \text{C} \cdot & \dots & \text{C} \cdot \text{O} \cdot \text{C} \cdot \text{O} \cdot \end{matrix}$  is proposed. Possible objection might be raised that free valencies are thus left at either end of the carbon chain; this would, however, only indicate the presence of two unsaturated positions in a highly complex molecule,

which would consequently be far less reactive than the simpler molecule. This accords well with the experimentally established fact that such polymerides are in general much less active than the simple substances, with which, however, they usually have certain actions in common.

H. W.

**Partial Condensation of Natural Gas at Liquid Air Temperatures and a Curious Effect Observed with the Nitrogen which Dissolves in the Condensate.** JOHN SATTERLY (*Trans. Roy. Soc. Canada*, 1919, 13, iii, 109—121).—Methods for the preliminary separation of natural gas by condensation are described. Sudden solution and expulsion of nitrogen by liquid methane occurred. [See *J. Soc. Chem. Ind.*, 1920, 539A.]

J. R. P.

**The Oxidation of Paraffins.** AD. GRÜN [with E. ULBRICH and TH. WIRTH] (*Ber.*, 1920, 53, [B], 987—996).—The recent publication of Kelber (this vol., i, 280) has induced the author to place on record some of the results obtained by himself.

Under suitable conditions, pure paraffins, or mixtures such as vaselin or petroleum, are readily oxidised to fatty acids by air or even by gaseous mixtures containing as little as 1% of oxygen. The statements by various authors that the process can be catalytically accelerated by suitable oxygen carriers are, in general, erroneous, and depend, in part at any rate, on insufficiently extended analyses of the products. Thus a series of experiments carried out with a paraffin, m. p. 52°, at 160° showed that metallic oxides, such as lime and barium oxide, salts with an alkaline reaction, and certain neutral substances, such as carbon and fuller's earth, are particularly harmful, whilst acidic substances, such as stearic acid, are, according to the properties of the hydrocarbon used, either helpful or at any rate not markedly inhibitive. If the conditions of reaction are not carefully chosen, one carbon atom after another of the intermediate products can be oxidised away, and the whole series of acids from those of high molecular weight to the volatile acids, and ultimately to formic acid or carbon dioxide, may be obtained. Particularly when oxygen is used, the action is likely to lead to violent explosions, due to the intermediate formation of peroxides.

The products of oxidation differ not only quantitatively, but also qualitatively, according to the conditions of experiment. The most interesting observation is that, when the conditions are not too vigorous, the product consists of mixtures of waxes with more or less free acid, alcohols, and some unsaponifiable matter. The composition of the mixture of acids depends entirely on factors, such as temperature, duration of action, etc., and may consist mainly of the series  $C_{16}$  to  $C_{22}$  or higher, or of such in which  $C_{10}$  to  $C_{14}$  or  $C_{15}$  predominate. Hydroxy-fatty acids are also formed, and are present partly in the form of esters or estolides, whilst unsaturated acids, probably derived from the hydroxy-acids by loss of water, are also found. The unsaponifiable matter consists

to a small extent of unchanged paraffin, but chiefly of higher alcohols with some carbonyl compounds. The separation of these products is a matter of difficulty, since the usual qualitative and quantitative carbonyl reactions are not trustworthy with substances of high molecular weight. Removal of the carbonyl derivatives is most readily effected indirectly by reducing them to alcohols by sodium and amyl alcohol, and their amount can be indirectly estimated by determining the hydroxyl number of the product before and after such treatment. They appear to consist of a mixture of aldehydes with certain amounts of ketones.

The results so far obtained do not permit any definite conclusion to be drawn with regard to the course of the oxidation; it would appear, however, that molecular oxygen attacks the carbon chain at a greater distance from the methyl group than is to be expected from analogous processes.

H. W.

#### Fatty Acids Obtained by the Oxidation of Paraffins.

FRANZ FISCHER and WILHELM SCHNEIDER (*Ber.*, 1920, 53, [B], 922—925).—Pure paraffin or crude expressed paraffin is heated with dilute sodium carbonate solution in a steel autoclave at about 170°, whilst simultaneously compressed air is pumped through the mixture. The paraffins are considerably more rapidly oxidised under these conditions than at atmospheric pressure, and the yield of fatty acids is as high as 90% of the paraffin used. The rate of reaction depends on the temperature in the usual manner, and is proportional to the pressure of the air. Iron, manganese, and copper have approximately equal catalytic effects, but the other substances investigated are less active, possibly in part owing to the catalytic activity of the steel walls of the autoclave. Under the same conditions, the quantity of fatty acids produced per hour is, within limits, proportional to the amount of paraffin, but the highest yields per given time are best obtained by working so as to secure complete neutralisation of the sodium carbonate solution rather than complete utilisation of the paraffin. Examination of the fatty acids, which are purified in the usual manner, shows that they are true, monobasic fatty acids, the density of which is less than unity, and that they dissolve completely in light petroleum; unlike the more common members, however, they contain an uneven number of carbon atoms. The following have been definitely characterised:  $C_{15}H_{30}O_2$ , m. p. 65°–66°;  $C_{17}H_{34}O_2$ , m. p. 58°–59°;  $C_{19}H_{38}O_2$ , m. p. 50°–51°;  $C_{21}H_{42}O_2$ , m. p. 38°.

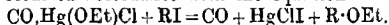
Re-examination of a patented process for the oxidation of paraffin by blowing air through the substance heated at 135–145° in an iron vessel in the absence of water shows that the actual products are the acid anhydrides, which can be separated from unaltered paraffin by taking advantage of the insolubility of the latter in acetone.

H. W.

**The Constitution of the Mercury Compounds of Carbon Monoxide and of Ethylene.** WILHELM MANCHOT (*Ber.*, 1920, 53, [B], 984–987).—The author's experiments (the full details



of which will be published elsewhere) lead him to the conclusion that the ethylene compounds mentioned in the title are to be regarded as additive products of ethylene and basic mercury salt,  $C_2H_4.Hg(OH)X$ , and not as structural compounds, as formulated by Schoeller, Schrauth, and Essers (A., 1913, i, 1162; this vol., i, 225). The close similarity between these substances and those given by carbon monoxide indicates a similar structure for the latter also. This conclusion is supported by the fact that methyl acetatomercuriformate yields carbon monoxide, mercury iodide, and mercury acetate when heated with methyl iodide at  $100^\circ$ , whereas, according to the structural formulation, mercuric iodide and methyl acetate would be expected; similarly, ethyl chloromercuriformate and *n*-propyl iodide yield carbon monoxide and mercury haloid without a trace of methyl butyrate. Reaction appears to occur in accordance with the equation



The mercury derivatives obtained by Schoeller and Schrauth by the action of ethylene on an alcoholic solution of mercury acetate behave similarly to those prepared in aqueous solution and also to the carbon monoxide compounds; in particular, they are extremely readily decomposed by halogen acids, with liberation of ethylene, whilst the latter is also evolved when they are treated with alkyl iodides. Their constitution may therefore be expressed by the formula  $C_2H_4.Hg(OEt)X$ . H. W.

**Preparation of Dimethylbutadiene.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.P. 319505; from *Chem. Zentr.*, 1920, ii, 776).—Pinacone chlorohydrin is treated with hydroxyl-free substances which can combine with acids, such as ammonia or organic bases. Thus, when it is distilled with dimethylaniline, a mixture of water and dimethylbutadiene passes over between  $60^\circ$  and  $80^\circ$ . H. W.

**Production of True Acetylenic Hydrocarbons from *epi*-Dibromohydrin.** R. LESPIEAU and BOURGUEL (*Compt. rend.*, 1920, 170, 1584—1586).—*epi*-Dibromohydrin,  $CH_3Br.CBr.CHBr$ , reacts in the cold with mixed magnesium derivatives to give compounds of the type  $CH_3.CBr.CH.R$ , which, when acted on by alcoholic potassium hydroxide, lose the elements of hydrogen bromide, giving an acetylenic hydrocarbon, but the action is complicated by the tendency of the triple linking to migrate. A better method is to prepare a tribromide from the compound,  $CH_3.CBr.CH_2Br$ , and then act on this with sodium ethoxide, the product being  $CHBr.CBr.CH_2R$ , which, when acted on by zinc in alcoholic solution, gives the required acetylenic hydrocarbon,  $CH.C.CH_2R$ . Thus *epi*-dibromohydrin condenses with magnesium ethyl bromide to give  $\beta$ -bromopentene, b. p.  $107$ — $108^\circ$ ,  $D_4^{20}$  1.277. This compound unites with bromine to give  $\alpha\beta$ -tribromopentane, b. p.  $108$ — $109^\circ$ ; 17 mm.,  $D_4^{20}$  2.03, which with sodium ethoxide yields  $\alpha\beta$ -dibromopentene, b. p.  $66$ — $67^\circ$ /19 mm.,  $D_4^{20}$  1.73. This compound, when

treated in alcoholic solution with zinc, gives  $\Delta^2$ -pentinene,  $\text{CH}_3\text{C}:\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$ .  
W. G.

**Production of Chloropicrin.** KENNEDY JOSEPH PREVITÉ ORTON and (SIR) WILLIAM JACKSON POPE (Brit. Pat. 142878).—Chloropicrin is obtained by the action of chlorine in presence of water on picric acid or other suitable nitrophenol, a sufficient amount of alkali, preferably sodium hydroxide or carbonate, being added either before or during the reaction to dissolve the nitro-compound and neutralise the acid produced according to the equation  $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH} + 11\text{Cl}_2 + 5\text{H}_2\text{O} = 3\text{CCl}_3\cdot\text{NO}_2 + 13\text{HCl} + 3\text{CO}_2$ . For example, 1 part of picric acid may be dissolved in a solution of 2.975 parts of sodium hydroxide in 50 parts of water, and, after cooling to 2–4°, whereby sodium picrate separates in small crystals, a slow, intermittent stream of chlorine is led in until the colour of the solution is discharged. The chloropicrin separates as an almost colourless oil, and amounts to 180–190% of the weight of picric acid taken.  
G. F. M.

**The Effect of Reducing Agents on Tetranitromethane, and a Rapid Method of Estimation.** AILEEN BAILLIE, ALEXANDER KILLEN MACBETH, and NORA IRÈNE MAXWELL (T., 1920, 117, 880–884).

**Corrections for Densities of Ethyl Alcohol to 15.5°/15.5°.** H. DROOP RICHMOND (*Analyst*, 1920, 45, 222).—A table is given showing the corrections to be made when the specific gravity is determined at temperatures between 10° and 25°, and for a range in specific gravity from 0.79 to 0.99.  
W. P. S.

**Preparation of Polyhydroxy-alcohols.** OSCAR MATTER (D.R.P. 299074; from *Chem. Zentr.*, 1920, iv, 14).—The requisite halogenated hydrocarbons are hydrolysed by aqueous solutions of carbonates or hydrogen carbonates, or mixtures thereof; as the reaction proceeds, the used hydrolysing agent is regenerated by addition of alkali hydroxide solution. Addition may be made periodically or continuously, at will or automatically. When using closed vessels, the concentration of the reagent may be maintained uniform during the whole experiment. The rate of reaction is thereby increased during the whole time, but particularly towards the end; concentrated products are obtained and the pressure in the vessel is lessened. The preparation of ethylene glycol from ethylene chloride and sodium carbonate or hydrogen carbonate at 130–140° is cited.  
H. W.

**A Hydrate of an Oxonium Compound.** O. MAASS and J. RUSSELL (*Trans. Roy. Soc. Canada*, 1919, 13, iii, 259–264).—A termolecular compound of ethyl ether, hydrogen bromide, and water was isolated by the freezing-point curves of the system  $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{HBr}$  and  $\text{H}_2\text{O}$ . The formula of the compound was found to be  $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{HBr}\cdot\text{H}_2\text{O}$ . The catalytic effect of mineral

acids in esterification is attributed to their linking the alcohol and organic acid in a molecular complex, where opportunity is afforded for interchange of radicles. A definite compound of ethyl alcohol and ethyl ether-hydrobromide could not be obtained. J. R. P.

**Preparation of Ethylene Oxide.** BADISCHE ANILIN- & SODA-FABRIK (D.R. P. 299682; from *Chem. Zentr.*, 1920, iv, 16).

— (i) Bases are added to warm ethylene chlorohydrin or its solutions. (ii) When bases other than alkalis are used, the order of addition of the substances may be changed. Excellent yields of ethylene oxide are obtained, whereas ethylene glycol and polyethylene glycols are mainly produced when the chlorohydrin is added to the warm alkali solution. H. W.

**The Xanthates of Cobalt and Nickel.** MARCEL DELÉPINE and LOUIS COMPIN (*Bull. Soc. chim.*, 1920, [iv], 27, 469–474. Compare this vol., i, 536. and Dubsky, A., 1914, ii, 732).

—These xanthates were prepared by double decomposition with alkali xanthates. The nickel salts crystallise much more readily than the cobaltic salts, the former being also more stable than the latter. As with the dithiocarbamates, there is a tendency to get some cobaltous salt along with the cobaltic salt, the tendency increasing with the molecular weight. The nickel salts are black, the cobaltic salts deep green or black, and the cobaltous salts brown. The salts described are *cobaltic methylxanthate*; *cobaltic* and *nickel ethylxanthates* (compare Dubsky, *loc. cit.*); *cobaltic* and *nickel n-propylxanthates*, *cobaltic* and *nickel n-butylxanthates* and *isobutylxanthates*; *cobaltic*, *cobaltous*, and *nickel isocamylxanthates*; *cobaltic* and *cobaltous benzylxanthates*; *cobaltic isopropylxanthate*; *cobaltic* and *nickel sec-butylxanthates*; *cobaltic* and *cobaltous menthylxanthates*. W. G.

**Trimethylsulphonium Compounds.** HILDEGARD BLÄTTNER (*Monatsh.*, 1919, 40, 417–429).—The author has prepared a number of double compounds formed from trimethylsulphine chloride, bromide, and iodide with a number of metallic salts. Methods are given for the preparation of methyl hydrogen sulphate and methyl sulphide.

Unlike methyl iodide, methyl chloride combines with difficulty with methyl sulphide, this combination not being aided materially by addition of zinc chloride or cadmium chloride, although the formation of double sulphinium compounds from metallic salt, sulphide, and alkyl haloid often proceeds considerably more readily than the union of sulphide and alkyl haloid alone. For the preparation of the other double chlorides, use was made, therefore, of trimethylsulphine chloride previously obtained.

Trimethylsulphine chloride is best obtained by treating an aqueous solution of the corresponding iodide with silver chloride; it decomposes at 100°, and has m. p. 100–117°.

*Bis(trimethylsulphine cupric chloride)*,  $(\text{SMe}_2)_2\text{CuCl}_2$ , forms orange-yellow crystals, which often and turn black at 180° and melt com-

pletely at 190°. *Bis(trimethylsulphine) zinc chloride*,  $(\text{SMe}_3)_2\text{ZnCl}_4$ , white, non-hygroscopic crystals, m. p. 208°. *Trimethylsulphine cadmium chloride*,  $\text{SMe}_3\text{CdCl}_3$ , white, non-hygroscopic needles or fan-like aggregates, subliming slightly, but not melting, at 430°. *Bis(trimethylsulphine) manganous chloride*,  $(\text{SMe}_3)_2\text{MnCl}_4$ , pale yellow, non-hygroscopic crystals, remaining unchanged at 300°. *Trimethylsulphine ferrous chloride*,  $\text{SMe}_3\text{FeCl}_3$ , m. p. (impure?) 190°. *Trimethylsulphine ferric chloride*,  $\text{SMe}_3\text{FeCl}_4$ , pale yellowish-brown crystals, softening at 240°, m. p. 250°. *Trimethylsulphine bismuth chloride* (?),  $\text{SMe}_3\text{BiCl}_4$  (?), white, crystalline precipitate. *Trimethylsulphine stannic chloride*,  $\text{SMe}_3\text{SnCl}_5$ , white precipitate, unmelted at 300°.

Trimethylsulphine bromide (compare Cahours, this Journ., 1875, 1181; 1876, i, 696; Carrara, A., 1892, 1422), readily obtained from the iodide and silver bromide, forms colourless, transparent, deliquescent plates, and begins to melt at 184° and volatilises completely at 189°. With copper bromide in methyl-alcoholic solution, it gives a deep violet precipitate, m. p. 184–185°. *Bis(trimethylsulphine) zinc bromide*,  $(\text{SMe}_3)_2\text{ZnBr}_2$ , forms white, non-hygroscopic crystals, m. p. 211–213°. *Trimethylsulphine cadmium bromide*,  $\text{SMe}_3\text{CdBr}_3$ , white, non-hygroscopic crystals, sinters at about 180°, m. p. (frothing) 233–235°. *Bis(trimethylsulphine) bismuth bromide*,  $(\text{SMe}_3)_2\text{BiBr}_3$ , pale yellow precipitate, swells at about 220°, m. p. 223°.

Trimethylsulphine iodide has m. p. 184–185° (compare Klinger, A., 1878, 128; Strömholm, A., 1900, i, 325). *Bis(trimethylsulphine) zinc iodide*,  $(\text{SMe}_3)_2\text{ZnI}_4$ , forms white, non-hygroscopic crystals, m. p. 183°. *Trimethylsulphine bismuth iodide*,  $\text{SMe}_3\text{BiI}_4$ , red salt, not melting at 290° (compare Vanino and Musgnug, A., 1917, i, 196). T. H. P.

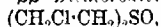
**Preparation of  $\beta\beta$ -Dichloroethyl Sulphide.** (SIR) WILLIAM JACKSON POPE, CHARLES STANLEY GIBSON, and HENRY FLEETWOOD THUILLIER (Brit. Pat. 142875).  $\beta\beta$ -Dichloroethyl sulphide is obtained in upwards of 90% yield by passing dry ethylene into sulphur monochloride heated to, and maintained at, 50–70°, until no further absorption occurs. The reaction is facilitated by introducing a small proportion of dichloroethyl sulphide into the sulphur monochloride before treatment with ethylene. The product is conveniently separated from the sulphur simultaneously formed by heating the reaction mixture to 100° and allowing to cool, when the sulphur is deposited in crystalline form and the supernatant liquid can be poured off. G. F. M.

**$\beta\beta$ -Dichlorodiethyl Sulphide and certain of its Derivatives.** WILHELM STEINKOPF, JULIUS HEROLD and JOSEPH STÖHR (Ber., 1920, 53, [B], 1007–1012).  $\beta\beta$ -Dichlorodiethyl sulphide,  $\text{S}(\text{CH}_2\text{CH}_2\text{Cl})_2$ , is readily prepared as a colourless oil, b. p. 108–109°/15 mm. (yield, 83%), by the action of thionyl chloride on  $\beta\beta$ -dihydroxydiethyl sulphide in the presence of chloroform. It is oxidised by hydrogen peroxide to the corresponding

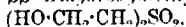
*sulphoxide*, m. p. 109°, and by potassium permanganate to the *sulphone*, colourless crystals, m. p. 48°, b. p. 179—181°/14—15 mm.  $\beta$ -Hydroxydiethyl sulphide,  $\text{SEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , b. p. 182—184°, is conveniently obtained by the addition of ethylene chlorohydrin to ethyl mercaptan dissolved in a solution of sodium in alcohol. It is converted by phosphorus tribromide into  $\beta$ -bromodiethyl sulphide, b. p. 83—86°/29 mm.  $\beta\beta'$ -Dibromo-diethyl sulphide, from  $\beta\beta'$ -dihydroxydiethyl sulphide and phosphorus tribromide, has b. p. 115.5°/1 mm., m. p. 31—34°.  $\beta\beta'$ -Dithiocyanodiethyl sulphide is prepared by heating the corresponding chloride with sodium thiocyanate in acetone solution; it forms bright yellow crystals, m. p. 35°.  $\beta\beta'$ -Dicyanodiethyl sulphide could not be prepared, but  $\beta\beta'$ -dicyanodimethyl sulphide, m. p. 47.5°, b. p. 177—178°/22 mm., was obtained by the action of potassium sulphide on chloroacetonitrile. *Phenyl  $\beta$ -chloroethyl sulphide*,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{SPh}$ , b. p. 144.5°/26 mm., 245°/atmospheric pressure, was prepared from ethylene chlorohydrin and thiophenol in the presence of a solution of sodium in ethyl alcohol. H. W.

#### Reactions and Derivatives of $\beta\beta'$ -Dichlorodiethyl Sulphide.

OREGON B. HELFRICH and E. EMMET REID (*J. Amer. Chem. Soc.*, 1920, **42**, 1208—1232).— $\beta\beta'$ -Dichlorodiethyl sulphoxide,



plates, m. p. 109.5°, is obtained by diluting a solution prepared by the addition of  $\beta\beta'$ -dichlorodiethyl sulphide to concentrated nitric acid at the ordinary temperature. On distillation, even under reduced pressure, it is partly decomposed into the sulphide, but it is unchanged by boiling water or silver nitrate solution; alcoholic sodium hydroxide converts it into *dihydroxydiethyl sulphoxide*,  $(\text{HO}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}$ , a viscous, oily liquid, easily soluble in water. The dichloro-compound apparently has no action on the skin, whereas *dichlorodiethylsulphone*,  $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{SO}_2$ , leaflets, m. p. 56°, b. p. 183°/20 mm., causes blisters and persistent sores, and also has a lachrymatory, and a slight sternutatory, effect. The physiological activity of these compounds appears to be parallel to the extent to which they suffer hydrolysis (compare Marshall, *J. Amer. Med. Assoc.*, 1919, **73**, 684), for the sulphone reacts partly with boiling aqueous silver nitrate solution. It is obtained from the sulphoxide by oxidation with fuming nitric acid, potassium permanganate, or, most satisfactorily, a solution containing 5—10% of chromic acid and 15—18% of sulphuric acid. The sulphone suffers decomposition at 230° when distilled under atmospheric pressure.  $\beta\beta'$ -Dihydroxydiethylsulphone,



is a viscous, somewhat deliquescent syrup, b. p. 140—165°/15 mm. Condensation products of the sulphide, sulphoxide, and sulphone with sodium salts of phenols, thiophenols, alcohols, mercaptans, and with aromatic amines have been prepared. *Di- $\beta$ -phenylthio-diethyl sulphide*,  $(\text{EPh}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ , m. p. 57.5°. *Di- $\beta$ -phenylthio-diethyl sulphoxide*,  $(\text{SPh}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}$ , m. p. 121.0°. *Di- $\beta$ -*

- phenylthioldiethylsulphone,  $(\text{SPh}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 104·5°.
- Di- $\beta$ -phenylsulphinyldiethyl sulphoxide,  $(\text{SOPh}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}$ , m. p. 161°.
- Di- $\beta$ -phenylsulphinyldiethylsulphone,  $(\text{SOPh}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 164°.
- Di- $\beta$ -phenylsulphonyldiethylsulphone,  $(\text{SO}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 235°.
- Di- $\beta$ -phenoxydiethyl sulphide,  $(\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ , m. p. 54·2°.
- Di- $\beta$ -phenoxydiethylsulphone,  $(\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 108°.
- Di- $\beta$ -p-tolyloxydiethyl sulphide,  $(\text{C}_6\text{H}_4\text{Me}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ , m. p. 78°.
- Di- $\beta$ -p-tolyloxydiethylsulphone,  $(\text{C}_6\text{H}_4\text{Me}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 120°.
- Di- $\beta$ -o-tolyloxydiethyl sulphide, m. p. 46·5°.
- Di- $\beta$ - $\alpha$ -naphthoxydiethyl sulphide,  $(\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ , m. p. 94·5°.
- Di- $\beta$ - $\beta$ -naphthoxydiethyl sulphide, m. p. 129°.
- Di- $\beta$ - $\beta$ -naphthoxydiethylsulphone,  $(\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 151°.
- Di- $\beta$ -vanilloxydiethyl sulphide,  $[\text{OMe}\cdot\text{C}_6\text{H}_3(\text{CHO})\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2]_2\text{S}$ , m. p. 131·5°.
- Di- $\beta$ -eugenoxdiethyl sulphide,  $[\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}_2\cdot\text{CH}_2]_2\text{S}$ , m. p. 113·5°.
- Di- $\beta$ -2:4:6-tribromophenoxydiethyl sulphide,  $(\text{C}_6\text{H}_2\text{Br}_3\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ , m. p. 118·5°.
- Di- $\beta$ -butylthioldiethyl sulphide,  $(\text{C}_4\text{H}_9\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ , m. p. 17·5°, b. p. 222—223°.
- Di- $\beta$ -butylthioldiethyl sulphoxide,  $(\text{C}_4\text{H}_9\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}$ , m. p. 25°.
- Di- $\beta$ -butylthioldiethylsulphone,  $(\text{C}_4\text{H}_9\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 73·7°.
- Di- $\beta$ -butylsulphinyldiethyl sulphoxide,  $(\text{C}_4\text{H}_9\cdot\text{SO}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}$ , m. p. 196°.
- Di- $\beta$ -butylsulphinyldiethylsulphone,  $(\text{C}_4\text{H}_9\cdot\text{SO}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 101°.
- Di- $\beta$ -butylsulphonyldiethylsulphone,  $(\text{C}_4\text{H}_9\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 266·5°.
- Di- $\beta$ -ethylthioldiethyl sulphide,  $(\text{SEt}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ , m. p. 17°, b. p. 173—175°.
- Di- $\beta$ -ethylthioldiethylsulphone,  $(\text{SEt}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 64°.
- Di- $\beta$ -ethylsulphonyldiethylsulphone,  $(\text{SO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 223°.
- Di- $\beta$ -methylthioldiethylsulphone,  $(\text{SMe}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 77°.
- Di- $\beta$ -propylthioldiethyl sulphide,  $(\text{SPr}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ , m. p. 27·5°, b. p. 193—195°.
- Di- $\beta$ -propylthioldiethylsulphone,  $(\text{SPr}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 75·5°.
- Di- $\beta$ -propylsulphonyldiethylsulphone,  $(\text{SO}_2\text{Pr}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 254°.
- Di- $\beta$ -isobutylthioldiethylsulphone,  $(\text{C}_4\text{H}_9\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 94·2°.
- Di- $\beta$ -sec-butylthioldiethylsulphone,  $(\text{C}_4\text{H}_9\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 15°.
- Di- $\beta$ -amylthioldiethyl sulphide,  $(\text{C}_5\text{H}_{11}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ , m. p. 20°.
- Di- $\beta$ -amylthioldiethylsulphone,  $(\text{C}_5\text{H}_{11}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 91°.
- 4-Phenyl-1:4-thiazan,  $\text{NPh}\langle\text{CH}_2\cdot\text{CH}_2\rangle\text{S}$ , m. p. 108—111°.
- 4-Phenyl-1:4-thiazan 4-oxide,  $\text{NPh}\langle\text{CH}_2\cdot\text{CH}_2\rangle\text{SO}$ , m. p. 123·5°.
- 4-p-Tolyl-1:4-sulphonazan,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\langle\text{CH}_2\cdot\text{CH}_2\rangle\text{SO}_2$ .

m. p. 136.5°. 4-*o*-Tolyl-1:4-sulphonazan, m. p. 135°. Di- $\beta$ -acetoxylethyl sulphide,  $(\text{OAc}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ , b. p. 155–156°/20 mm.,  $D_{20}^{20}$  1.132,  $n_D^{22.5}$  1.4720. Of the compounds,  $(\text{R}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S}$ , only those could be obtained in which R = aromatic radicle.

$\beta\beta'$ -Di-iododiethyl sulphide,  $(\text{CH}_2\text{I}\cdot\text{CH}_2)_2\text{S}$ , m. p. 55–60°, the sulphoxide,  $(\text{CH}_2\text{I}\cdot\text{CH}_2)_2\text{SO}$ , m. p. 104.5°, and the sulphone,  $(\text{CH}_2\text{I}\cdot\text{CH}_2)_2\text{SO}_2$ , m. p. 203°, were obtained from the chloro-derivatives and sodium iodide.

A report on the physiological activity of the above compounds, which is in general slight, is included in the paper. J. K.

**Ethylene Sulphide,  $\text{C}_2\text{H}_4\text{S}$ .** MARCEL DELÉPINE (*Compt. rend.*, 1920, 171, 36–38).—Chloroethyl thiocyanate is decomposed by an aqueous solution of sodium sulphide, giving sodium thiocyanate, sodium chloride, and ethylene sulphide,  $\begin{matrix} \text{CH}_2 \\ \diagup \\ \text{CH}_2 \end{matrix} \text{S}$ , a colourless liquid, b. p. 55–56°,  $D_4^{20}$  1.0368–1.0342,  $n_D^{20}$  1.4914–1.49001. The material slowly polymerises spontaneously, and very rapidly in the presence of some reagents, to give a white solid. With methyl iodide, it gives a crystalline compound having all the characteristics of a sulphinium iodide. This iodide with silver chloride gives a crystalline chloride, yielding a platinumchloride. W. G.

**Organic Derivatives of Tellurium. II. Constitution of the Dimethyltelluronium Dihaloids.** RICHARD HENRY VERNON (*T.*, 1920, 117, 889–898).

**Production of Acetic Acid from Paracetaldehyde as the Primary Material.** SOCIÉTÉ DES ACIÉRIES & FORGES DE FIRMIXY (*Brit. Pat.* 121195).—Paracetaldehyde is directly converted into acetic acid by electrolytic oxidation, using a porous cathode, for example, gas carbon, and a refractory anode, such as magnetite or platinum. The electrolyte consists of 10% sulphuric acid, in which the paracetaldehyde dissolves to the extent of 10–15%. Any excess is allowed to float on the surface, and dissolves as the oxidation proceeds. Oxidation is facilitated by the addition to the bath of a small quantity of a salt of a metal capable of a plurality of degrees of oxidation, such as manganese, cerium, molybdenum, or vanadium. A high current density is employed, and the acetic acid is allowed to accumulate to a concentration of about 40%, when it is separated from the sulphuric acid by distillation. G. F. M.

**Manufacture of Ethyl Acetate from Paracetaldehyde as the Primary Material.** SOCIÉTÉ DES ACIÉRIES & FORGES DE FIRMIXY (*Brit. Pat.* 131600).—By adding to the mixture of acetic acid and dilute sulphuric acid produced by the electrolytic oxidation of paracetaldehyde (preceding abstract) a quantity of ethyl alcohol equivalent to the acetic acid which it contains, and distilling the whole on a rectifying apparatus, esterification is effected, and pure ethyl acetate distils. The liquid remaining containing

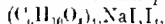
sulphuric acid and a little non-esterified acid and alcohol may be again employed as a basis for a fresh electrolysis. G. F. M.

**Poly-iodide Compounds of Oxalic Esters.** ANTON SKRABAL and ELEONORE FLACH (*Monatsh.*, 1919, **40**, 431–444).—The authors have prepared a number of compounds analogous to the double compound of potassium periodide and ethyl oxalate (compare Skrabal, A., 1917, i, 378) and differing essentially only in degree of stability. These compounds mostly crystallise well and always exhibit a dark colour and metallic lustre, which is frequently combined with pleochroism. They exhibit the characters of the poly-iodides, including the tendency to decompose with liberation of iodine; the pressure at which such decomposition occurs furnishes a measure of the stability.

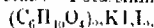
Study of the dissociation equilibria of these compounds shows that the tendency of the iodides of the alkali metals to form compounds with iodine and ethyl oxalate increases in passing from sodium to potassium and then diminishes in passing to rubidium and caesium, ammonium occupying a position near that of potassium; the sodium compound does not correspond in composition with the others. Further, a poly-iodide compound with a bromide as component is of far lower stability than that with the corresponding iodide as component.

The compounds, which have all been prepared either in aqueous solution or in presence of water, apparently belong to the oxonium compounds, but it is undecided whether it is the carbonyl or the ethereal oxygen atom of the oxalic ester which assumes the oxonium valencies. The following compounds are described:

*Compounds of ethyl oxalate: Sodium periodide compound,*

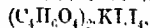


small, reddish-brown crystals. *Potassium periodide,*

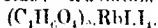


small, brown to violet, highly stable crystals (*loc. cit.*). *Rubidium periodide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_2 \cdot \text{RbI}_2$ , dark brown crystals with metallic lustre. *Ammonium periodide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_2 \cdot \text{NH}_4\text{I}_2$ , bluish-black crystals with metallic lustre, highly stable. *Caesium periodide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_2 \cdot \text{CsI}_2$ , shining, dark brown crystals. *Potassium perbromide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_2 \cdot \text{KBr}_2$ , unstable, shining, golden-brown scales. *Sodium mercuric periodide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_4 \cdot 3\text{NaI} \cdot \text{HgI}_2 \cdot \text{I}_4$ , reddish-brown crystals, readily emitting iodine. *Potassium mercuric periodide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_4 \cdot 4\text{KI} \cdot \text{HgI}_2 \cdot \text{I}_8$ , reddish-brown crystals. *Potassium cadmium periodide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_4 \cdot 6\text{KI} \cdot \text{CdI}_2 \cdot \text{I}_{10}$ , shining, brownish-green crystals, readily losing iodine. *Potassium bismuth periodide*,  $(\text{C}_6\text{H}_{10}\text{O}_4)_6 \cdot 3\text{KI} \cdot \text{BiI}_3 \cdot \text{I}_6$ , reddish-brown powder. In all these compounds, one molecule of ethyl oxalate corresponds with one atom of periodine.

*Compounds of methyl oxalate: Potassium periodide,*



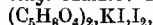
shining, bluish-black crystals. *Rubidium periodide,*





dark crystals. In these compounds, one molecule of the methyl ester corresponds with two atoms of periodine.

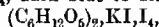
*Compounds of methyl ethyl oxalate: Potassium periodide,*



brown crystals. *Rubidium periodide,*  $(C_5H_6O_4)_2, RbI, I_2$ , dark brown crystals. *Ammonium periodide,*  $(C_5H_6O_4)_2, NH_4I, I_2$ , dark blue crystals.

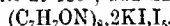
*Compounds of tetraethyl semi-ortho-oxalate: Potassium periodide,*  $(C_{10}H_{20}O_5)_2, KI, I_2$ , brownish-violet, stable crystals.

*Compounds of tetramethyl semi-ortho-oxalate: Potassium periodide,*  $(C_6H_{12}O_5)_3, 2KI, I_4$ , dark blue to black crystals, and



brownish-black powder, readily emitting iodine. T. H. P.

**Periodides of Carbonyl Compounds.** A. M. CLOVER (J. Amer. Chem. Soc., 1910, 42, 1248—1260. Compare A., 1904, i, 322).—Reviewing the isolated instances in the literature of periodides derived from organic compounds free from nitrogen, the author concludes that it is the carbonyl group which is essentially involved in their structure, and suggests the designation "carbonyl periodides," including among them the periodides of dimethyl- and tetramethyl-pyrones, and of amides, and anilides. Coumarin potassium periodide (Dox and Gaessler, A., 1917, i, 346. Compare Morgan and Micklethwait, T., 1906, 89, 866) is best purified by the addition of ether to its concentrated solution in alcohol or ethyl acetate, and has the formula  $(C_9H_6O_2)_3, 2KI, I_5, H_2O$ . *Methyl oxalate potassium periodide,*  $(C_4H_6O_4)_2, KI, I_5$ , separates from a mixture of aqueous solutions of its components as fine crystals with a dark bluish-grey lustre, m. p. 55—75°. Benzamide potassium periodide (Moore and Thomas, A., 1914, i, 1130), after crystallisation from ether, melts at 130°, and has the formula



*Succinimide potassium periodide,*  $(C_4H_5O_2N)_4, KI, I_2$ , m. p. 141—149°, separates as light brown, lustreless crystals from an alcoholic solution of its components. Succinic anhydride potassium periodide,  $(C_4H_4O_3)_4, KI, I_2$ , previously described (*loc. cit.*), separates as crystals with a green lustre from a mixture of ethyl acetate and chloroform. From barbituric acid, two compounds result, according to the proportions of the components mixed in aqueous solution; in one case, yellow crystals,  $(C_4H_4O_3N_2)_2, 2KI, I_5$ , in the other, green crystals,  $(C_4H_4O_3N_2)_2, 2KI, I_5$ , are obtained. *Diethyl-barbituric acid potassium periodide,*  $(C_8H_{12}O_5N_2)_2, KI, I_4$ , from aqueous solutions of its components, forms crystals with a steel-blue lustre, m. p. above 200°. In other cases, there is evidence of formation of compounds, although they cannot be isolated. Thus many organic ketones, anhydrides, esters, etc., dissolve iodine and potassium iodide to a considerable extent, although the solubility of each of these is limited. In this manner, acetone furnishes dark green, needle-shaped crystals of a potassium iodide periodide, and needles with a golden lustre of a sodium iodide periodide. Also, often as a result of fusion or grinding together of the com-

ponents, a strong metallic lustre is developed, and iodine is not so readily lost by volatilisation from the product; in other cases, a lustrous residue is left on evaporation of a solution of the components.

J. K.

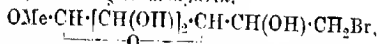
**The Tartaric Acid Compounds of Antimony.** A. BLANCHETIÈRE (*Bull. Soc. chim.*, 1920, [iv], 27, 477—490).—The velocity of solution of freshly-prepared antimony hydroxide in a solution of tartaric acid agrees with Jungfleisch's theory of esterification and not with the formation of a salt. This action, relatively rapid at first, diminishes in velocity very quickly when the ratio of tartaric acid to antimony hydroxide dissolved is about two, but the solution will proceed until this ratio becomes one, after a very long time. Using *d*-tartaric acid, these solutions, when evaporated, give syrupy solutions, which only crystallise with difficulty. If racemic acid is used, the material can be separated, by evaporation, into monoantimonyltartaric acid and ill-defined products. The best method of preparation of this acid is to extract the complexes, richer in tartaric acid, with acetone. Precipitation methods only give a hydrophile gel of the required acid containing a varying excess of tartaric acid.

W. G.

#### Compounds and Derivatives of *d*-Glucose-6-bromohydrin.

EMIL FISCHER, RICHARD HELFERICH, and PAUL OSTMANN (*Ber.*, 1920, 53, [B], 873—886).—It is shown that many of the reactions of acetylbromoglucose can be extended to acetyldibromoglucose and that, under suitable conditions, compounds are formed which retain the terminal bromine atom in the place of the hydroxyl group of the sugar molecule. The configuration of all these compounds is the same as that of *d*-glucose.

*B*-Methyl-*d*-glucoside- $\zeta$ -bromohydrin,



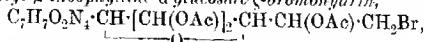
prisms, m. p. about 148° (decomp.),  $[\alpha]_D^{25} - 35.12^\circ$  in aqueous solution, is obtained by the action of a methyl-alcoholic solution of ammonia on triacetylmethylglucoside-6-bromohydrin. It is hydrolysed by *N*-hydrochloric acid with the formation of  $\zeta$ -bromoglucose, which, however, could only be obtained as a syrup, but could be identified by conversion into *d*-glucose-ethylmercaptal- $\zeta$ -bromohydrin, long, silky needles, m. p. 107° (corr. decomp.),  $[\alpha]_D^{25} + 4.92^\circ$  in alcoholic solution.

*Tetra-acetyl-d*-glucose- $\zeta$ -bromohydrin, needles or four-sided prisms, m. p. 127° (corr.) after previous softening, is prepared by treating a hot solution of acetyldibromoglucose in glacial acetic acid with dry silver acetate.

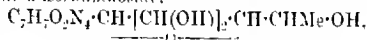
Acetyldibromoglucose is converted, when boiled with water, into a mixture of  $\zeta$ -bromoglucose (identified as the ethylmercaptal) and anhydroglucose (compare Fischer and Zach, A., 1912, i, 239, 678), which was isolated from the product in the form of its *p*-bromophenylhydrazone, pearly leaflets, m. p. 184° (corr.) after slight previous softening, to a reddish-brown syrup; the substance

exhibits mutarotation when dissolved in dry pyridine,  $[\alpha]_D^{16}$  having the initial and final values  $-18.89^\circ$  and  $-10.86^\circ$  respectively. It is decomposed by formaldehyde, yielding anhydroglucose, m. p.  $118^\circ$  (corr.),  $[\alpha]_D + 51.4^\circ$ , whereas Fischer and Zach give  $+53.7^\circ$ .

*Triacetyl- $\beta$ -theophylline-d-glucoside- $\zeta$ -bromohydrin*,

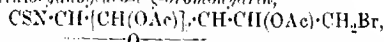


is prepared from acetyldibromoglucose and the silver derivative of theophylline in boiling xylene solution and forms slender needles, m. p.  $193-194^\circ$  (corr.),  $[\alpha]_D^{18} - 9.92^\circ$  in tetrachloroethane solution. It is hydrolysed by methyl-alcoholic ammonia to  *$\beta$ -theophylline-d-glucoside- $\zeta$ -bromohydrin*, coarse prisms,  $+2.5\text{H}_2\text{O}$ ; the anhydrous substance has m. p. about  $217^\circ$  (decomp.) after slight softening,  $[\alpha]_D^{18} - 18.99^\circ$  in aqueous solution,  $[\alpha]_D^{18} - 13.87^\circ$  in *N*-hydrochloric acid solution, mutarotation not being observed in either instance. The triacetyl compound is reduced by zinc dust and acetic acid to *triacetyl- $\beta$ -theophylline-d-isorhamnoside*, m. p.  $230^\circ$  (corr.), after slight previous softening, which does not exhibit appreciable optical activity when dissolved in tetrachloroethane or glacial acetic acid; it is transformed by a solution of ammonia in methyl alcohol into  *$\beta$ -theophylline-d-isorhamnoside*.



m. p.  $254^\circ$  (corr.),  $[\alpha]_D^{18} - 22.27^\circ$  in aqueous solution.

*Triacetylthiocyanoglucose- $\zeta$ -bromohydrin*,



slender, interwoven needles, m. p.  $164.5^\circ$  (corr.) after previous softening,  $[\alpha]_D^{18} + 16.14^\circ$  in tetrachloroethane solution, is prepared from acetyldibromoglucose and silver thiocyanate, and is converted by boiling alcohol into *triacetyl-d-glucosethiourethane- $\zeta$ -bromohydrin*,  $\text{OEt} \cdot \text{CS} \cdot \text{NH} \cdot \text{CH} \cdot \underset{\text{O}}{\underset{|}{\text{CH}}}(\text{OAc})_2 \cdot \text{CH} \cdot \text{CH}(\text{OAc}) \cdot \text{CH}_2\text{Br}$ , thin,

silky leaflets, m. p.  $128-129^\circ$  (corr.),  $[\alpha]_D^{18} + 10.27^\circ$  in tetrachloroethane solution. H. W.

### Biochemical Preparation of Sucrose from Gentianose.

EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1920, 171, 11-15).—By the action of emulsin, freed as completely as possible from invertase, on a solution of gentianose, a mixture of dextrose and sucrose was obtained. The dextrose was converted into  $\beta$ -methyl glucoside and the sucrose isolated in a pure crystalline state.

W. G.

### The Action of Radium Radiation on Sucrose and Agar.

A. FERNAC (*Biochem. Zeitsch.*, 1920, 102, 246-251).—Sucrose is inverted by the action of radium radiation. Agar submitted to the same influence liquefies with the production of sugars (most probably galactose and arabinose) which reduce strongly Fehling's solution. The chemical change in both cases is due to the primary action of the radium.

S. S. Z.

**Alteration of Volume in the Inversion of Sucrose.** N. SCHOORL (*Zeitsch. Nahr. Genussm.*, 1920, **39**, 113—121).—A discussion on the contraction in volume occurring when sucrose is hydrolysed by acid. The contraction for one gram-molecule of sucrose and one gram-molecule of water is 6.9 c.c., which corresponds approximately with 0.5 c.c. for 26 grams of sucrose per 100 c.c. of water.  
W. P. S.

**The Hydrolysis of the Polysaccharides.** E. HILDT (*Compt. rend.*, 1920, **170**, 1505—1507. Compare A., 1919, ii, 84).—A further examination of the use of the mixture of sulphuric acid and sodium benzenesulphonate in the molecular proportions of 1:2 for the hydrolysis of disaccharides. It is shown that both dextrose and galactose are unaltered by this reagent, retaining their rotatory and reducing powers. Non-levulosic sugars, such as lactose, maltose, or glycogen, are not hydrolysed at the ordinary temperature by this catalyst, but in the case of sugars, such as sucrose, raffinose, or inulin, the levulose is completely split off after the lapse of a considerable time at the ordinary temperature, or in less than one hour at 95—98° in the case of sucrose and raffinose.  
W. G.

**Iron Salt of Carbohydrate-Phosphoric Acid.** KARL SCHWIZER (*Mitt. Lebensmit. Hyg.*, **11**, 16—23; from *Chem. Zentr.*, 1920, i, 881).—*Iron zymophosphate*,  $C_6H_{10}O_4(PO_3Fe)_2$ , is a greyish-green, tasteless, and odourless powder, which decomposes without melting at 200°. For its preparation, a solution of sucrose (100 grams) in distilled water (250 c.c.) is treated with commercial expressed yeast (150 grams) and toluene (1 c.c.); after ten minutes, a solution of disodium phosphate (80 grams) in water (300 c.c.) is added, and, after four hours, the yeast is removed, preferably by centrifuging. The liquid is heated to 60°, and, after removal of precipitated albumin, is treated with a saturated solution of ferrous chloride (14 grams). The separation of the precipitate is facilitated by the addition of an equal volume of alcohol (90%) to the solution; it is purified by repeated grinding with water. The salt is decomposed by hydrochloric, nitric, sulphuric, and acetic acids, the iron passing thereby into the ionised state; with sodium hydroxide, a precipitate of iron hydroxide is formed. The salt is decomposed in the stomach, both iron and phosphoric acid being converted into forms which are readily absorbed.

H. W.

**Hydrogen Peroxide as Solvent.** MAX BAMBERGER and JOSEF NUSSBAUM (*Monatsh.*, 1919, **40**, 411—416). Concentrated aqueous hydrogen peroxide solutions, and in higher degree the almost anhydrous peroxide obtained from these by freezing, serve as excellent solvents for many organic compounds. Among the latter are compounds rich in hydroxyl groups, and the higher the molecular weight of these compounds, the more concentrated must be the peroxide solution necessary to effect solution.

For instance, 60% aqueous hydrogen peroxide solution dissolves

starch, giving solutions which are viscous or dough-like, according to the concentration. Cellulose and its decomposition products are also soluble, and the less the extent to which the cellulose has been altered, the greater the concentration of the peroxide required for solution. From these solutions, precipitants, such as water, throw out the cellulose in chemically modified form, and the solutions themselves undergo gradually increasing change in properties. Cellulose wool, as used for preparing cellulose nitrate, dissolves to the extent of 25%, the tenacious dough thus formed becoming more and more mobile when kept out of contact with atmospheric moisture. The products precipitated from these solutions differ from those obtained by the action of sulphuric acid on cellulose, no substance coloured blue by iodine being formed.

With peroxide solution weaker than that necessary for solution, cellulose swells, and cotton wool thus treated shows under the microscope swollen fibres with a greatly diminished lumen; flattened or damaged portions of the fibres dissolve the more readily, the double refraction and the visibility of the fibres disappearing as dissolution proceeds.

In spite of its negative heat of formation, anhydrous hydrogen peroxide is not explosive, and a large quantity of it cannot be exploded by means of a 2-gram mercury fulminate cap. In conjunction with certain organic compounds, however, the peroxide yields powerful explosives capable of technical application.

Sugars and proteins also dissolve in concentrated hydrogen peroxide solutions. The latter produce no apparent change in pure, white wool, but when this is withdrawn and well washed with water, the fibres exhibit considerable strength, and are almost as elastic as rubber; after being dried, these fibres completely lose their elasticity.

The action of the peroxide on substances dissolved in it seems to be of the nature of a decomposition or depolymerisation. Thus paraformaldehyde yields formaldehyde, or, under some conditions, formaldehyde peroxide (compare Legler, A., 1883, 860; 1886, 327; Nef, A., 1898, i, 111).

In working with concentrated hydrogen peroxide solutions, great cleanliness is necessary, since contamination with catalysts, for instance, iron, manganese, or lead, causes very vigorous decompositions, which are accompanied by generation of heat, and may produce ignition. Such mixtures burn in the air with hissing, like smokeless powder. Ignition may be produced by sprinkling powdered lead peroxide or iron pyrites on the peroxide solution.

T. H. P.

### **Constitution of Cellulose. I. Acetolysis of Ethyl Cellulose.**

KURT HESS and WALTER WITTELSNACH (*Zeitsch. Elektrochem.*, 1920, 26, 232—251).—The various formulæ proposed for cellulose are discussed. The formation of *o*-bromo-5-methylfurfuraldehyde from cellulose and from dextrose (Fenton and Gostling, T., 1901, 79, 361, 807) suggests that, contrary to the formulæ of Green (T., 1906, 89, 811), cellulose contains dextrose residues in the same

form as dextrose itself. The production of levoglucosan from starch as readily as from cellulose, to which it bears no resemblance (Pictet and Sarasin, A., 1918, i, 58), discounts the idea of any constitutional similarity between levoglucosan and cellulose, but suggests that it owes its origin to dextrose residues present in each. In confirmation of the view that the hydrofuran ring of levoglucosan is not present in cellulose, it is shown that ethyl cellulose, on distillation under reduced pressure, gives no ethyl levoglucosan, but only a small proportion of an oily product. As a basis for a new formula for cellulose, it is pointed out that all five hydroxyl groups of dextrose are etherifiable, as evidenced by the tannins (E. Fischer, A., 1913, i, 1352; 1919, i, 278) and certain disaccharides (Haworth and Leitch, T., 1918, 113, 188; 1919, 115, 809; Irvine and Dick, T., 1919, 115, 593). Formulae, too complicated to be reproduced, are therefore discussed in which the hydroxyl groups of a dextrose or cellobiose molecule are etherified by molecules of dextrose or cellobiose. In order to reach some decision between the numerous possibilities of such an arrangement, the work of Ost (A., 1906, i, 560) and of Madsen (*Diss.*, Hanover, 1917) on the production of cellobiose acetate and dextrose penta-acetate is reviewed, in conjunction with a repetition of their experiments. The conclusion is that the probable maximum yield of each from ten parts of air-dry cellulose is 6.2 grams of cellobiose acetate and 12 grams of dextrose penta-acetate. It has not been possible to attain the higher yields recorded by Ost in certain experiments. The dextrins, which occur in the form of acetates when the maximum proportion of cellobiose acetate is not reached, are looked on as mixed partial degradation products of the cellulose molecule, resulting from the removal by hydrolysis in a variety of ways of one or more dextrose or cellobiose residues. The formula  $\text{OX}\cdot\text{CH}\cdot\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{[CH(ON)}\text{]}_2\cdot\text{CH}\cdot\text{CH(ON)}\cdot\text{CH}_2\cdot\text{OX}$ , in which X represents the residue,  $\text{CH}\cdot\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{[CH(ON)}\text{]}_2\cdot\text{CH}\cdot\text{CH(OH)}\cdot\text{CH}_2\cdot\text{OH}$ , requires that

9.38 grams of cellulose should give 6.42 grams of cellobiose acetate and 12.51 grams of dextrose penta-acetate, whilst the other alternatives require widely different quantities. Although the arbitrary nature of this formula, in view of the evidence available, is recognised, it is adopted as a working basis. In accordance with it, Denham and Woodhouse (T., 1913, 103, 1735; 1914, 105, 2357) considered dextrose to be among the products of hydrolysis of methyl cellulose. Evidence of a similar nature is presented from the results of hydrolysis of an ethyl cellulose, containing 2.5 ethyl groups per dextrose residue (or 3 per residue with free hydroxyl groups in the formula), under conditions of acetolysis much milder than those usual in the case of cellulose, and such that hydrolysis of ethoxy-groups, as might occur with hydrochloric acid, did not occur. It follows from the formula that the ethoxy-numbers of the ethyl dextrins produced in the form of acetates as intermediate products of acetolysis will always be less than that of the original ethyl cellulose, and, a point not explained by previous

formule, when degradation has proceeded sufficiently far, less than that of the ethyl glucoses, which, in the form of acetates, will also have a lower ethoxy-number than ethyl cellulose. Repeated experiments uniformly confirmed this, and the ethoxy-number of the sugar portion at the outset (36.5) was much higher than that for diethyl triacetylglucose (21.6%), the formation of which the older formulae would suggest. The marked difference between cellulose and its derivatives, for example, nitrate, acetate, and the products obtained by the action of acids, alkalis, or zinc or copper ammonium compounds, is accounted for by considering such derivatives to be derived from the above simple formula, which is taken as representing hydrocellulose (for which the name cellulose is now proposed), whilst cellulose is a condensation product of a number of such molecules. The results of Stern (T., 1904, 85, 336), Stein (*Diss.*, Dresden, 1911), and Ost (A., 1913, i, 833) show that little, if any, elimination of water can be assumed in this condensation, and it is suggested that the separate molecules are united through residual affinities of hydroxyl groups. The ability of alcohols of all kinds (Grün and others, A., 1908, i, 934; 1910, i, 352; Vanino and Hartl, A., 1906, i, 785), of dextrose (Lippmann, *Chemie der Zuckerarten*, I, 549), and of its esters and glucosides (Fischer and Hess, A., 1912, i, 415) to form double compounds with metallic salts is in accord with this idea, which leads to a simple explanation of the disintegrating effect of zinc chloride, ammonia, and similar reagents on cellulose as due to their competition for the residual valencies responsible for the complexity of the cellulose molecule. Ethyl cellulose is a derivative of cellulose, since its acetolysis takes place under much less stringent conditions than that of cellulose, and the heat of reaction is slight; the contrast in this respect with cellulose is only partly accounted for by the greater number of hydroxyl groups in cellulose, and is chiefly due to the difference in distribution of valency in the two cases. It is also suggested that the physical characteristic of cellulose as a hollow thread is reproduced in the arrangement of the cellulose molecules in the cellulose complex, and that this complex may be partly broken down by mechanical means, for example, in the case of "totgemahlener" cellulose, which represents a stage of disintegration approaching the less profound of those produced chemically. Similar considerations may apply to the molecules of hemicelluloses, protein, and caoutchouc, but the case of starch is left open. J. K.

**Cellulose and its Esters. I. Fractional Precipitation of Cellulose Nitrates.** J. DECLAUX and (MME) E. WOLLMAN (*Bull. Soc. chim.*, 1920, [iv], 27, 411-420).—By fractional precipitation of cellulose nitrate from its solution in acetone by aqueous acetone or water, it is possible to divide it into a number of fractions which have widely different viscosities in 2% acetone solution. By repeating this process with the extreme fractions, fractions were ultimately obtained the viscosities of which in acetone solution were as 46:1, and at one end a cellulose nitrate was obtained which in

5% acetone solution was as viscous as glycerol. These various fractions have not undergone any change in the fractionation, since they obey the law of mixtures in so far as their viscosities are concerned. Further, the nitrogen content of the different fractions of one and the same operation is sensibly the same. A better method of separation of the fractions rather than by fractional precipitation is probably by the use of a series of ultra-filters. The different cellulose nitrates can best be characterised and differentiated by osmotic pressure measurements. W. G.

**The Viscosity of Solutions of Nitrocellulose in Mixtures of Acetone and Water.** IRVINE MASSON and ROBERT McCALL (*T.*, 1920, 117, 819—823).

**The Viscosity of Solutions of Cellulose Nitrate in Ether-Alcohol.** WILLIAM HOWIESON GIBSON and ROBERT McCALL (*J. Soc. Chem. Ind.*, 1920, 39, 172—176r).—With a given cellulose nitrate, the viscosity of its solution in an ether-alcohol mixture is dependent on the ratio of ether to alcohol, and reaches a minimum value at a definite ratio. This optimum ratio is independent of the concentration of the cellulose nitrate, but is affected by the nitrogen content.

The optimum composition of an ether-alcohol solvent for a cellulose nitrate is not affected by the addition of glyceryl nitrate. Glyceryl nitrate, when added to solutions of cellulose nitrate in ether-alcohol, tends to increase the viscosity of the solution. W. G.

**Measurement of the Viscosity of Pyroxylin Solutions.** E. F. HIGGINS and E. C. PITMAN (*J. Ind. Eng. Chem.*, 1920, 12, 587—591).—Efflux viscosimeters are only suitable for pyroxylin solutions of low viscosity, and the steel ball viscosimeter (*T.*, 1920, 117, 473) for those of very high viscosity. The most generally applicable instrument is Stormer's viscosimeter, in which the viscosity is calculated from the speed of rotation of a cylinder in the liquid. When absolute viscosities are plotted as ordinates against the times of 100 revolutions as abscissae, the points will be found to lie along a straight line. The equation is therefore of the type  $\eta = At - B$ , where  $B$  is the value of  $\eta$  when  $t = 0$ . In the case of the particular instrument used, when  $t = 0$ ,  $\eta = -25 = B$ . By substituting this value for  $B$  at any point of the curve, the value for  $A = 4.6$ . The equation for calculating absolute viscosity from the observed readings when a 150-gram counterweight was used was therefore  $\eta = 4.6t - 25$ . The speed of revolution varies directly with the magnitude of the counterweight. The correction for the friction factor is practically a constant over a viscosity range of 20 to 500 centipoises. C. A. M.

**The Neutral Hydrolysis of Guncotton. The Alkaline Hydrolysis of Guncotton.** E. KNECHT and B. R. BOSROCK (*J. Soc. Chem. Ind.*, 1920, 39, 163—165r).—When guncotton is heated with water in a sealed tube at 190°C, it undergoes hydrolysis, the



guncotton disappearing and a pale straw-coloured liquid being left. The rate of hydrolysis depends on the relative proportions of guncotton and water used. If the temperature is lowered by more than about  $2^{\circ}$ , the hydrolysis is extremely slow, and if it is raised  $10-15^{\circ}$ , a considerable amount of charring takes place. The amount of gas given off by heating 0.5 gram of guncotton with 25 c.c. of water for half-an-hour at  $190^{\circ}$  is 99 c.c. The gas consists of carbon monoxide and dioxide and nitrous oxide and nitrogen. Some hydrocyanic acid and ammonia are found in the solution. Of the 13.05% of nitrogen originally present in the guncotton, 10.24% is found as nitrous oxide and nitrogen, 0.43% as hydrogen cyanide, 1.20% as ammonia, 0.12% as nitrate, and 0.27% undetermined.

When guncotton is dissolved in aqueous sodium hydroxide on a water-bath, it is found that 65% of the total nitrate nitrogen is reduced to nitrite in order to provide the oxygen for the organic oxidation products which result from the hydrolysis. The extent of this reduction is nothing like so great in the alkaline hydrolysis as in the neutral aqueous hydrolysis.

W. G.

**Non-existence of Valence and Electronic Isomerism in Hydroxylammonium Derivatives.** ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1920, **42**, 1232-1245).—A theoretical paper in which the alkyl hydroxylammonium salts are discussed with regard to their formation and constitution. The author comes to the conclusion that since isomeric trialkyl-hydroxylammonium salts and trialkyl-dialkylhydroxylammonium derivatives are unknown, there is no experimental evidence in this field to support Werner's ammonium or co-ordination hypotheses, or any modification of them. Neither are any facts known which substantiate electronic conceptions, or the existence of "electromers" in this group of compounds.

J. F. S.

**Salts of N-Methylhexamethylenetetramine.** R. TSCHUNKKE (U.S. Pat. 1336709).—Salts of N-methylhexamethylenetetramine are produced by treating a mixture of formaldehyde and ammonia with methylating agents (such as methyl sulphate, methyl thiocyanate, methyl nitrate, methylamine thiocyanate, or chlorobromomethane) in the presence of acid anions, heating for some time, and allowing the product to crystallise. The thiocyanate, metaborate, dichromate, ferrocyanide, picrate, perchlorate, chlorate, nitrate, sulphate, acetate, and salicylate are mentioned, and details of the methods of making them are given.

CHEMICAL ABSTRACTS.

**The Metallic Dithiocarbamates, especially those of Cobalt and Nickel.** LOUIS COMPIN (*Bull. Soc. chim.*, 1920, [iv], 27, 464-469. Compare Delépine, *Ibid.*, 1908, [iv], 3, 613).—The author has prepared certain dithiocarbamates of cobalt, nickel, and copper by double decomposition of salts of these metals with the sodium dithiocarbamates. The cobaltic salt obtained is always accompanied by a certain amount of cobaltous salt, and in one or two cases it was possible to isolate the latter salts. The following

salts were prepared: *Sodium, cobaltic, and nickel methylthiocarbamates; sodium and cobaltic ethylthiocarbamates; sodium, cobaltic, and nickel propylthiocarbamates.* These sodium and nickel salts were all crystalline, but the cobaltic salts were only obtained with difficulty. *Copper dimethylthiocarbamate; cobaltic, nickel, and copper diethylthiocarbamates; potassium cobaltic, nickel, and copper dipropylthiocarbamates; cobaltic diallylthiocarbamate; cobaltic di-isobutylthiocarbamate; cobaltic, cobaltous, nickel, and copper di-isoamylthiocarbamates; potassium, cobaltic, and cobaltous dibenzylthiocarbamates; sodium and cobaltic methylphenylthiocarbamates; sodium and cobaltic piperidylthiocarbamates; and cobaltic tetrahydroisquinolylthiocarbamate.*

W. G.

**Is the Direct Synthesis of Carbamide by Urease Possible?**  
 TH. J. F. MATTAAR (*Rec. trav. chim.*, 1920, **39**, 495—498).—The author has repeated Barendrecht's work (this vol., i, 195) on the action of the urease in soja flour on ammonium carbonate, and has also used a sample of urease prepared by the method of van Slyke and Cullen (*A.*, 1914, ii, 822), and finds no evidence that the synthesis of carbamide takes place; but, on the contrary, finds that any carbamide introduced into such a solution of ammonium carbonate containing the urease is destroyed.

W. G.

### Arsine Thiocyanates and certain other Organic Derivatives of Arsenic.

WILHELM STEINKOPF and WALTER MIEG (*Ber.*, 1920, **53**, [B], 1013—1017).—Attempts have been made to prepare arsine thiocyanates of the general form,  $RAs(SCN)_2$  and  $R_2AsSCN$ , by the action of solutions of sodium thiocyanate in acetone on the corresponding chlorides. Under these conditions, methylarsine dichloride gave only products which were extremely readily decomposed by moisture with the production of amorphous, yellow substances, and which could not be distilled even under diminished pressure, whilst arylarsine dichlorides could not be caused to react in the desired sense. On the other hand, products of the type  $R_2AsSCN$ , in which R is an alkyl or aryl radicle, could be obtained in several cases as fairly stable substances. Improved methods of preparing some arsine chlorides are given and certain new members of this series are described.

Ethylchloroarsine, b. p. 145—150°, is conveniently prepared from arsenic trichloride and mercury diethyl, and is converted by potassium hydroxide in the presence of benzene and a little water into ethylarsine oxide,  $AsEt_2O$ , colourless oil, b. p. 158°/10 mm., which readily becomes oxidised on exposure to air. *iso-Amlydichloroarsine*, from *iso*amylarsinic acid and phosphorus trichloride in chloroform solution, is a colourless liquid, b. p. 88.5—91.5°/15 mm., which is decomposed by water. *α-Naphthyl*dichloroarsine has m. p. 68°. Cacodyl chloride is obtained by the action of sodium hypophosphite on cacodylic acid in the presence of concentrated hydrochloric acid, and has b. p. 106.5—107°; it does not fume on

exposure to the atmosphere, and is rapidly converted by dry air into a crystalline oxidation product. *Cucodyl thiocyanate*,  $\text{AsMe}_3\cdot\text{SCN}$ , b. p.  $92^\circ/17$  mm., is a colourless oil which gradually becomes yellow when preserved. *Phenyldimethylarsine dichloride*,  $\text{AsMe}_2\text{PhCl}_2$ , m. p.  $134^\circ$  (decomp.), is prepared by the addition of chlorine to phenyldimethylarsine and is decomposed at  $180^\circ$ , yielding *phenylmethylchloroarsine*, b. p.  $229-232^\circ$ . *Diphenylarsine thiocyanate* has b. p.  $230-233^\circ/22-23$  mm.; it is decomposed by water with the elimination of the thiocyno-group.

H. W.

**Chemical Actions of Penetrating Radium Radiation. XI. Influence of Penetrating Rays and of Ultra-violet Light on Toluene alone and in Presence of Water.** ANTON KAILAN (*Monatsh.*, 1919, 40, 445-466. Compare A., 1918, i, 209).—

Exposure of toluene in the dark for about two years to the action of the radiation from a preparation containing 0.080 gram of radium in a glass envelope 1 mm. in thickness, results in attack of less than 0.25% of the toluene, the products formed including benzaldehyde, benzoic acid, and apparently formic acid. The increase in the density of the toluene and the weight of the residue left on evaporation indicate that the principal product of the reaction consists, not of benzoic acid, but of a yellow, viscous mass composed presumably of hydrocarbons and of condensation products of benzaldehyde (compare Gamician and Silber, A., 1912, i, 174). Changes of similar nature and order of magnitude are produced in toluene, exposed for twenty-two hours to the radiation from a quartz mercury lamp at a distance of 8-9 cm.

The action of radium radiation on toluene in presence of water yields three times as much acid as in absence of water, benzoic and formic acids being produced, together with a non-acid residue. As regards the action on toluene of the radiation from a quartz mercury lamp, this is not increased by the presence of water to the same extent as the action of radium radiation, but oxalic acid is then produced, as well as benzoic and formic acids. T. H. P.

**The Catalysing Action of Aluminium in the Preparation of Chlorobenzenes.** JEAN MECNIER (*Compt. rend.*, 1920, 170, 1451-1452).—In the preparation of chlorobenzene, one part of aluminium to one thousand of benzene acts as a very satisfactory catalyst, the absorption of chlorine proceeding smoothly. The action should be stopped when the density of the liquid reaches 1.008.

W. G.

**The Replacement of Substituents in the Benzene Nucleus.** A. F. HOLLEMAN and A. J. DEN HOLLANDER (*Rec. trav. chim.*, 1920, 39, 435-480. Compare A., 1916, i, 22; 1918, i, 216).—The eleven dichlorodinitrobenzenes have been prepared and their behaviour in the presence of sodium methoxide studied. Three of these compounds are new.

By hydrolysis of 3:6-dichloro 2-nitroacetanilide, and subsequent

replacement of the amino-group by a nitro-group by the method of Körner and Contardi (compare A., 1914, i, 263), 1:4-dichloro-2:3-dinitrobenzene, m. p. 103°, is obtained, which is identical with Jungfleisch's  $\beta$ -dichlorodinitrobenzene obtained in the preparation of 1:4-dichloro-2:6-dinitrobenzene (compare *Ann. Chim. Phys.*, 1868, [iv], 15, 259).

1:4-Dichloro-2:5-dinitrobenzene, m. p. 119°, is prepared by the hydrolysis of 3:6-dichloro-4-nitroacetanilide, and replacement of the amino-group by a nitro-group. Alternatively, this compound may be prepared by nitrating 4-chloro-3-nitroacetanilide, hydrolysing the product, diazotising the amine, and introducing a chlorine atom by the Gattermann reaction. The authors consider that the compounds described under the name 1:4-dichloro-2:5-dinitrobenzene by Morgan and Newman (T., 1902, 81, 1378, 1382), Hartley and Cohen (T., 1904, 85, 868), and Nason (A., 1919, i, 10) are either impure or different isomerides.

By the chlorination of 2:5-dinitroaniline by hydrochloric acid and potassium chlorate, a mixture of two compounds, which were not isolated, was obtained. This mixture was diazotised, and the resulting diazonium salts submitted to the Gattermann reaction. By this means, 1:4-dichloro-2:5-dinitrobenzene mixed with a small amount of 1:2-dichloro-3:6-dinitrobenzene, m. p. 60°, was obtained. Several attempts to prepare the last-named compound by other methods were unsuccessful.

From a qualitative and quantitative study of the action of sodium methoxide on the chloronitrobenzenes, it is shown that the activity of a replaceable chlorine atom is increased considerably by the introduction of a nitro-group into the para- or ortho-positions, and that the activity of a nitro-group becomes greater on the introduction of a chlorine atom, more particularly in the meta-position. The introduction of a second nitro-group into the chloronitro- and dichloronitrobenzenes renders the chlorine atoms in the meta-position to the nitro-group already present inactive. On the other hand, when the two nitro-groups are in a meta-position to one another, it is always a chlorine atom which is attacked.

W. G.

**Nitration of *m*-Nitrotoluene.** M. D. MARQUERYOL, M. G. A. KOEHLER, and JOVINET (*Bull. Soc. chim.*, 1920, [iv], 27, 420--424).

-By the nitration of *m*-nitrotoluene with a mixture of 16 parts of sulphuric acid (96%) and 2.25 parts of nitric acid (88%) for eight hours at 100°, a mixture of three trinitrotoluenes, namely, 2:3:4-, 3:4:6-, and 2:3:6- or 2:3:5-trinitrotoluenes, is obtained.

W. G.

**Influence of Nitro-groups on the Reactivity of Substituents on the Benzene Nucleus. II. The Dinitrotoluenes.** JAMES KESSER and MICHAEL PARKIN (T., 1920, 117, 852-859).

**2:3:6-Trinitrotoluene: a New Synthesis.** OSCAR LISLE BRADY and ARTHUR TAYLOR (T., 1920, 117, 876-880).

**Trinitration of *o*-Xylene.** M. D. MARQUETROL and P. LORIETTE (*Bull. Soc. chim.*, 1920, [iv], 27, 424—426).—By passage through its mono- and dinitro-derivatives without purification of these, but using fresh nitration mixtures at each stage, the two trinitro-*o*-xylenes, previously described by Crossley and Renouf (compare T., 1909, 95, 202), were obtained from *o*-xylene. W. G.

**Preparation of Condensation Products from *N*-Arylsulpho-derivatives of Aromatic Aminosulphonic Acids.** SOCIETY OF CHEMICAL INDUSTRY IN BASEL (D.R.-P. 319713; from *Chem. Zentr.*, 1920, ii, 777).—Formaldehyde is caused to react with *N*-arylsulphonyl derivatives of aminosulphonic acids of the benzene or naphthalene series. Examples are given of the condensation of *p*-toluenesulphonylsulphanilic acid in sodium carbonate solution, of *p*-toluenesulphonyl-1-aminonaphthalene-6-sulphonic acid in dilute sodium carbonate solution, and of amino-*p*-toluenesulphonyl-1-aminonaphthalene-6-sulphonic acid in acetic acid solution with formaldehyde. The products are soluble in water, precipitate albumin, and tan hide. H. W.

**The Constitution of Anthracene.** K. VON AUWERS (*Ber.*, 1920, 53, [B], 941—944).—During recent years, a variety of chemical evidence in favour of the orthoquinonoid structure of anthracene has been adduced, and this is now supplemented by physical evidence. If this mode of formulation be correct, the system would contain a continuous chain of four conjugated double bonds which could not neutralise one another, and although this system is twice broken, and by reason of its position in the rings would probably not exhibit its full activity, it should, nevertheless, show strong exaltation of the refractive and the dispersive power. On the other hand, a compound with a para-linking in the central ring should show, at most, little exaltation, since the benzene nuclei are so disposed that active conjugations are not existent, and the para-bond is known in analogous cases to have little, if any, effect. Anthracene itself is unsuitable for investigation on account of its high melting point, but 9-*iso*amylanthracene has been investigated and found to exhibit very marked optical exaltation, which is very much less in evidence in the case of its dihydro-derivative, which behaves precisely as if it contained two benzene nuclei.

The following constants are recorded: 9-*iso*Amylanthracene, m. p. 58°, (i)  $D_4^{25}$  0.9982,  $n_D^{25}$  1.62353,  $n_D^{55}$  1.63475,  $n_D^{65}$  1.67008, (ii)  $D_4^{25}$  0.9987,  $n_D^{25}$  1.62491,  $n_D^{55}$  1.63636,  $n_D^{65}$  1.67152. Dihydro-9-*iso*amylanthracene, (i) b. p. 202°/23 mm.,  $D_4^{25}$  1.0022,  $D_4^{55}$  1.025,  $n_D^{55}$  1.56091,  $n_D^{65}$  1.56584,  $n_D^{75}$  1.58047, (ii) b. p. 201—205°/17 mm.,  $D_4^{25}$  0.9940,  $D_4^{55}$  1.016,  $n_D^{55}$  1.55791,  $n_D^{65}$  1.56261,  $n_D^{75}$  1.57651,  $n_D^{85}$  1.5736. H. W.

**Derivatives of Acenaphthene.** KARL FLEISCHER and PAUL WOLFF (*Ber.*, 1920, 53, [B], 925—931).—The recent publication of Mayer and Kaufmann (this vol., i, 301) on a similar topic has

caused the authors to communicate the results obtained by themselves in this field.

A *diacetylacenaphthene*, colourless needles, m. p.  $146^{\circ}$ , has been isolated from the less volatile products obtained in the preparation of 5-acetylacenaphthene. The latter readily condenses with benzaldehydes to yield well-crystallised benzylidene derivatives, of which the *o*-chlorobenzylidene compound forms yellow prisms, m. p.  $113^{\circ}$ . 5-Acetylacenaphthene is reduced to 5-ethylacenaphthene, colourless, mobile oil, b. p.  $158^{\circ}/13$  mm., m. p.  $42.5-43^{\circ}$ , D  $1.0407$ ,  $n$   $1.6117$ , by amalgamated zinc and hydrochloric acid (compare Mayer and Kaufmann, *loc. cit.*). The latter condenses with acetyl chloride in the presence of aluminium chloride to yield 6(?)*acetyl*-5-ethylacenaphthene, m. p.  $110.5^{\circ}$ , which gives nicely crystalline benzylidene derivatives with aromatic aldehydes, and is reduced by Clemmensen's method to 5:6(?)*di*-ethylacenaphthene, pale yellow oil, b. p.  $182^{\circ}/14$  mm., m. p.  $10-11^{\circ}$ .

The author's attempts to introduce a second ethylene bridge in the *peri*-position in the acenaphthene molecule date back to 1911; for this purpose, oxalyl chloride does not appear to be a suitable reagent, but better results can be obtained with oxalyl bromide, which yields the substance (annexed formula), yellow crystals, m. p.  $226^{\circ}$  after slight previous softening and darkening. (The authors propose to call the substance *pyracene*, *miquinone* and the parent hydrocarbon *pyracene*.)

Bromoacetyl bromide condenses with acenaphthene in the presence of aluminium chloride to yield 5-bromo-*acetylacenaphthene*, pale grey, crystalline powder, m. p.  $180^{\circ}$ , and a substance, small, yellow needles, m. p.  $94-96^{\circ}$ , which could not be definitely identified.

A hydrocarbon closely allied to the hypothetical pyracene has been isolated by the reduction, by phosphorus and hydriodic acid, of 2:2-diethyl*peri*-acenaphthindan-1:3-dione (Freund and Fleischer, A., 1910, i, 490; 1913, i, 1073), which yields 2:2-diethyl*peri*acenaphthindane (annexed formula), centimetre-long crystals, m. p.  $93-95^{\circ}$ .

H. W.

**New Synthesis of Perylene.** FRITZ HANSBERG and ALOIS ZINKE (*Monatsh.*, 1919, 40, 403-404).—Perylene may be obtained in good yield by heating 2:2'-dihydroxy-1:1'-dinaphthyl to a high temperature ( $400-500^{\circ}$ ) with a halogen compound of phosphorus ( $\text{PCl}_5$ ,  $\text{PCl}_3$ ,  $\text{POCl}_3$ ,  $\text{PBr}_3$ ), addition of phosphorous acid being of advantage. Hydrogen phosphide and small proportions of free phosphorus are formed during the reaction.

T. H. P.

**New Derivatives of Perylene.** ALOIS ZINKE and ERNA UNTERREUTER (*Monatsh.*, 1919, 40, 405-410).—*Perylene hexa-*

*hydride*,  $C_{20}H_{18}$ , prepared by heating perylene with hydriodic acid and red phosphorus at  $200-210^\circ$ , forms almost colourless, rhombohedral plates, m. p.  $183-184^\circ$  (uncorr.), which gradually turn yellow, especially in the light. It appears to sublime unchanged when very cautiously heated, but yields perylene when distilled over heated asbestos. It dissolves in warm concentrated sulphuric acid, giving a red solution.

*Trinitroperylene*,  $C_{20}H_9(NO_2)_3$ , prepared by the action of nitric acid (D 1.10) at  $100^\circ$ , crystallises in needles, decomposes at about  $365^\circ$ , and yields a violet-red solution in warm, concentrated sulphuric acid.

*Tetranitroperylene*,  $C_{20}H_8(NO_2)_4$ , prepared by boiling perylene with concentrated nitric acid (D 1.4), forms deep brick-red leaflets and darkens at above  $300^\circ$ . With warm sulphuric acid, it gives a red solution.

The oxidation of perylene to perylenequinone is effected readily by boiling the hydrocarbon with aqueous chromic acid solution.

*Perylenequinol dibenzoate*,  $C_{20}H_{10}O_2Bz_2$ , prepared from perylenequinone by Scholl and Mansfeld's method (A., 1910, i. 494), forms bundles of yellow needles, m. p.  $295-296^\circ$  (uncorr.), and yields a reddish-yellow solution with concentrated sulphuric acid.

*Dibromoperylenequinone*,  $C_{20}H_8O_2Br_2$ , crystallises in needles or leaflets, decomposes at about  $412^\circ$ , and dissolves in concentrated sulphuric acid to a violet-red solution.

*Nitroperylenequinone*,  $C_{20}H_9O_2NO_2$ , forms brownish-red needles and exhibits no sharp melting point. It colours cotton violet and gives a violet-red solution in concentrated sulphuric acid. Its bromo-derivative,  $C_{20}H_8O_2BrNO_2$ , forms red needles and dyes cotton brown.

T. H. P.

**The Determination of the Relative Strengths of some Nitrogen Bases of the Aromatic Series and of some Alkaloids.** FRANCIS ARNALL (T., 1920, 117, 835-839).

**Preparation of Methyl Derivatives of Arylamino-compounds.** ALPHONSE MAILHE (Brit. Pat. 124219).—Mono- and dimethylated arylamines are obtained by passing a mixture of the vapours of the arylamine and methyl alcohol over a suitable catalyst, preferably precipitated alumina, at a temperature of  $350-400^\circ$ , condensing the product, and separating the methylated bases from the condensate. The catalyst is conveniently spread on trays or plates arranged in a series of tubes built into a suitable furnace. The mixture of mono- and dimethylarylamines produced by this process may, if desired, be converted entirely into the dimethylated amine by passing the vapour mixed with a further quantity of methyl alcohol a second time over the catalyst. The exhausted catalyst can be regenerated by calcination in air. Examples are given of the preparation of the mono- and dimethyl-anilines, -toluidines, -xyldines, and -naphthylamines. G. F. M.

**The Sulphonation of *m*-Sulphanilic Acid.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1920, **39**, 499–504).—The author confirms Schultz's view (*A.*, 1906, i, 837) as to the composition of the disulphonic acid obtained by the sulphonation of 3-aminobenzene-1-sulphonic acid by Limpricht and Drebes (*Ber.*, 1876, **9**, 552). When the aminobenzenedisulphonic acid is diazotised in hydrochloric acid solution and then treated with copper, on neutralising the solution with potassium hydroxide, *potassium 2-chlorobenzene-1,4-disulphonate* is obtained, which yields *2-chlorobenzene-1:4-disulphonyl chloride*, m. p. 96.5–97°. This acid chloride, when heated in a sealed tube with phosphorus pentachloride for four hours at 210°, gives 1:2:4-trichlorobenzene, m. p. 17–18°.

W. G.

**Vanillylamine.** E. K. NELSON (U.S. Pat. 1329272).—An alcoholic solution of vanillin is treated with hydroxylamine hydrochloride and sodium carbonate, the excess of alcohol is evaporated after keeping in a warm place for twenty-four hours, and vanillin-oxime is precipitated by water. The oxime in alcoholic solution is reduced by 2.5% sodium amalgam with the gradual addition of glacial acetic acid to maintain an acid reaction. Vanillylamine is then isolated as the hydrochloride.

CHEMICAL ABSTRACTS.

**Some Observations on the "Springing" of "Carbolate" and the Recovery of Phenol from the Resulting Aqueous Layer.** H. M. DAWSON (*J. Soc. Chem. Ind.*, 1920, **39**, 151–152r).—The loss of phenol in the aqueous layer when a solution of sodium phenoxide is neutralised by sulphuric acid is minimised by keeping the volume of the aqueous layer as small as possible, and thereby increasing the salting-out effect of the sodium sulphate. The percentage loss can be calculated from the formula

$$p = 75.5 (10^{10} \times \text{conc.}) C_2$$

where  $C_2$  is the concentration of sodium sulphate (anhydrous) in grams per litre. Experiments were made to recover the phenol from the aqueous layer by extracting with different organic solvents. When 50 grams of the solvent were shaken at 35° with a litre of a solution containing 10 grams of phenol and 200 grams of sodium sulphate, *o*-cresol and *m*-cresol each extracted 75% of the phenol, nitrobenzene 65%, benzene 41%, solvent naphtha (b. p. 145–155°) 40%, and light petroleum (b. p. 95–100°) 4.7%.

E. H. R.

**Esterification with Phenols.** M. BARONIN and F. GIORDANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1916, [iii], **22**, 125–134).—The interaction of a phenol and an anhydride serves as a general method for preparing esters in good yields. Various esters have been prepared in this way and their melting points determined by means of Pomilio's apparatus, in which electrical heating is employed.

With quinol and acetic anhydride, the product obtained forms white, micaceous scales, m. p. 119.4°, the reaction being greatly facilitated by the presence of a small proportion of phosphoric oxide, fuming sulphuric acid, or ferric or zinc chloride. These



condensing agents appear to exert, not a dehydrating action, but a catalytic effect, probably of ionic character (compare Bakunin, A., 1916, ii, 421).

The acetyl derivatives of the three nitrophenols are obtained by boiling together the phenol (1 mol.) and acetic anhydride (1 mol.) for ten to fifteen minutes, the presence of fused sodium acetate (compare Noeltling, Grandmougin, and Michel, A., 1893, i, 90) being unnecessary. Acetyl-*p*-nitrophenol has m. p.  $78.2^{\circ}$ , and *m*-nitrophenyl acetate,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OAc}$ , crystallises in straw-yellow, shining needles, m. p.  $53.5^{\circ}$ .

The acetyl derivatives of the three hydroxybenzoic acids may be prepared similarly (compare Oddo and Manuelli, A., 1897, i, 180), the melting points being  $137^{\circ}$ ,  $124.1^{\circ}$ , and  $180.5^{\circ}$  for the ortho-, meta-, and para-compounds respectively. Here also phosphoric oxide, fuming sulphuric acid, and zinc chloride act as catalysts, but the actions are not so energetic as with the dihydroxybenzenes and require initial heating.

Phenyleinnamic anhydride,  $(\text{C}_{15}\text{H}_{11}\text{O})_2\text{O}$ , obtained by boiling the acid with phosphoric oxide in chloroform solution (compare Bakunin, *loc. cit.*), forms crystals, m. p.  $120.5^{\circ}$ , and gives rather low values for the molecular weight in freezing benzene, owing possibly to the presence of a little unchanged acid or to dissociation of the anhydride. The phenyleinnamyl derivatives of the three dihydroxybenzenes,  $\text{C}_6\text{H}_3\text{O}_2(\text{C}_{15}\text{H}_{11}\text{O})_2$ , have the melting points  $154.2^{\circ}$ ,  $162.4^{\circ}$ , and  $230^{\circ}$  for the ortho-, meta-, and para-compounds (compare Bakunin, *loc. cit.*) respectively.

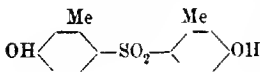
T. H. P.

**Preparation of Derivatives of *N*-Acylated *p*-Aminophenols.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 318803, additional to D.R.-P. 316902; from *Chem. Zentr.*, 1920, iv, 15).—*N*-Acyl derivatives of the urethanes of *p*-aminophenols are treated with  $\alpha$ -bromodiethylacetyl haloids. The preparation of the bromodiethylacetylurethane of *p*-acetylaminophenol from *p*-acetylaminophenylurethane, m. p.  $181^{\circ}$ , is described. The latter is obtained from guaiacolurethane and *p*-acetylaminophenol by distillation of the guaiacol at  $150^{\circ}$  or by reduction of *p*-nitrophenylurethane, m. p.  $161^{\circ}$ , by hydrogen in the presence of colloidal palladium. *p*-Aminophenylurethane hydrochloride has m. p. about  $235^{\circ}$  after softening above  $200^{\circ}$ , and is acetylated by a mixture of sodium acetate, acetic acid, and acetic anhydride.

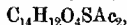
H. W.

***m*-Hydroxytolylsulphones.** JOSEF ZEHENTER (*Monatsh.*, 1919, 40, 377—389).—The action of sulphuric acid (about 30%  $\text{SO}_3$ ) on *m*-cresol at  $140^{\circ}$  yields the following two *m*-hydroxytolylsulphones, the  $\beta$ -compound being formed in small proportion.

**$\alpha$ -*m*-Hydroxytolylsulphone** (unmixed constitution) crystallises in plates or prisms ( $+\frac{1}{2}\text{H}_2\text{O}$ ), m. p.  $115-116^{\circ}$ , and dissolves readily in alkali hydroxides or ammonia, giving solutions from which it is precipitated by addition of acid.



Its *tetrabromo*-derivative,  $C_{14}H_{10}O_4Br_4S$ , forms almost colourless, acicular crystals, m. p.  $225^\circ$ . Its *diacetyl* compound,



forms prismatic, often crossed, crystals, m. p.  $142^\circ$ , and its *dibenzoyl* derivative,  $C_{14}H_{12}O_4SBz_2$ , groups of radiating, prismatic crystals, m. p.  $153-154^\circ$ . When the sulphone is heated with chromic acid in presence of water, an odour of *p*-benzoquinone is emitted, whilst oxidation with concentrated nitric acid yields 4:6-trinitrocresol.

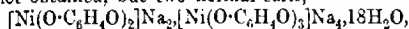
$\beta$ -m-*Hydroxytolylsulphone*, for which various constitutional formulæ are proposed, crystallises with 1MeOH in shining, colourless prisms, m. p.  $196-197^\circ$ , and in a current of air sublimes unchanged at  $180-200^\circ$ . The *diacetyl* derivative,  $C_{14}H_{12}O_4SAc_2$ , forms intergrown, prismatic crystals, m. p.  $197^\circ$ , and the *dibenzoyl* compound,  $C_{14}H_{12}O_4SBz_2$ , microscopic, prismatic crystals, m. p.  $194-225^\circ$ .

Together with these two sulphones, the action of sulphuric acid on *m*-cresol yields 3-cresol-6-sulphonic acid and another cresol-sulphonic acid, probably 3-cresol-2(or 4)-sulphonic acid, the *barium* ( $+H_2O$ ) and *potassium* ( $+2\frac{1}{2}H_2O$ ) salts of which were analysed.

T. H. P.

#### Compounds of Bivalent Cobalt and Nickel with Catechol.

II. R. F. WEINLAND and ANNA DÖTTINGER (*Zeitsch. anorg. Chem.*, 1920, 111, 167-174. Compare A., 1918, i, 298).—In an analogous manner to that previously adopted, the authors have prepared a basic sodium salt of cobalto-catechol of the formula  $2[Co(O\cdot C_6H_4O)_2]Na_3\cdot 3NaOH\cdot 14H_2O$ . In the case of nickel, a basic salt was not obtained, but two normal salts,

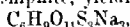


in thin, bluish-green leaflets, and  $[Ni(O\cdot C_6H_4O)_2]Na_3\cdot 12H_2O$ , in thick, dark green tablets. A further cobalt derivative of catechol is obtained by heating a solution of cobalt acetate and catechol; this compound crystallises in blue needles, and has the formula  $CH_3CO_2Co\cdot O\cdot C_6H_4\cdot OH\cdot H_2O$ . Attempts to prepare a similar nickel derivative failed, but a green powder of the formula  $Ni_2(C_6H_4O_2)_2(OH)_2\cdot 5H_2O$  was obtained.

J. F. S.

#### Tautomerism of Phenols. II.? Resorcinol. WALTER FUCHS

and BENNO ELSNER (*Ber.*, 1920, 53, [B], 886-898. Compare this vol., i, 159).—Resorcinol slowly reacts with a boiling aqueous solution of sodium hydrogen sulphite, yielding a *substance*,



which, in all probability, is the sodium salt of the bisulphite compound of 3:5-diketocyclohexanesulphonic acid, the formation of which can be explained by the assumption that resorcinol reacts in its tautomeric form. It loses a molecule of sulphur dioxide almost instantaneously, even in aqueous solution; a second molecule is eliminated more slowly and with much greater difficulty, whilst the third molecule is only lost to a slight extent even after protracted treatment. When it is allowed to remain for some time

in contact with an aqueous solution of sodium hydroxide at the ordinary temperature, it yields *sodium dihydroresorcinolsulphonate*, colourless needles, which is freely soluble in water and does not give precipitates with the salts of the heavy metals. With ferric chloride, an intense violet-red coloration is developed. It does not show the usual reactions of resorcinol. It is oxidised by potassium permanganate to oxalic acid. It readily absorbs bromine, but simultaneously becomes extensively decomposed, with formation of bromoform. *Dihydroresorcinolsulphonic acid* forms colourless crystals, m. p.  $172^{\circ}$ – $175^{\circ}$  (decomp.). The barium salt is also described. Resorcinol is the main product of the fusion of the latter with potassium hydroxide, whilst also sulphurous acid is removed. The constitution of the sulphonic acid has not been definitely elucidated, but the reaction just described indicates that the sulphonic group is in close proximity to a methylene group, since it is otherwise difficult to explain how a dihydroxylated cyclic sulphonic acid could yield resorcinol with elimination of sulphur dioxide; it appears most probable that the acid has a symmetrical structure.

H. W.

**The Action of an Alcoholic Solution of Potassium Hydroxide in the Presence of Zinc Powder on the Bromobenzhydrols and on some of their Derivatives.** P. J. MONTAGNE (*Rec. trav. chim.*, 1920, **39**, 492–494).—When the bromobenzhydrols or their derivatives are boiled with an alcoholic solution of potassium hydroxide in the presence of zinc powder, the bromine is completely replaced by hydrogen, but little or no resinous material is formed.

W. G.

**Polymorphism of Cholesterol Crystals.** A. RICHAUD (*Compt. rend. Soc. Biol.*, 1920, **83**, 389–391; from *Chem. Zentr.*, 1920, i, 896).—When a solution of cholesterol in hot acetic acid is evaporated, the substance is not infrequently deposited in radiating clusters instead of long needles arranged in crosses; the transformation into rhombic plates by addition of a drop of alcohol does not invariably occur.

H. W.

**Preparation of Metacholesterol.** ISAAC LIFSCHÜTZ (D.R.-P. 318900, 318901; from *Chem. Zentr.*, 1920, iv, 16).—1. Cholesterol or substances containing cholesterol are treated with mild oxidising agents until the formation of oxidation products of cholesterol can just be detected by the acetic-sulphuric acid reaction. *Meta-cholesterol* forms silvery leaflets, m. p.  $140^{\circ}$ – $141^{\circ}$ ; it does not give a coloration with ferric chloride or acetic-sulphuric acid. Its acetyl and benzoyl derivatives also differ from those of cholesterol or oxycholesterol. A solution of metacholesterol in alcohol, after addition of water and removal of alcohol by boiling, gives a perfectly uniform, more or less opalescent, colloidal solution, which can dissolve fats, higher alcohols, etc. Metacholesterol, when melted to the extent of 2% with fats or oils or with vaselin, allows the addition of more than 500% of water.

11. Metacholesterol is obtained from animal matter containing cholesterol (i) by treating the cholesterol substances with solvents according to known processes, whereby the cholesterol is separated in the solid form, and by suitable treatment of the filtrates, preferably by concentration, precipitating metacholesterol, leaving practically only oxysterol in solution; (ii) by treating the mixture with volatile substances and water or with the latter alone, dialysing or filtering the liquid, and fractionating the dissolved matter for the purpose of removing the substances which have smaller power of uniting with water according to (i). Considerable amounts of metacholesterol are contained in ox brain, and more in the blood fat. The great capacity of metacholesterol of mixing with water makes it suitable for the preparation of ointments, cosmetics, emulsions, and similar fatty mixtures with a very high water content.

H. W.

**The Polyacid Salts of Monobasic Acids: Sodium Tribenzoate.** PHILIPPE LANDRIEU (*Compt. rend.*, 1920, 170, 1452—1454).—Benzoic acid gives an acid sodium salt having the composition  $C_6H_5 \cdot CO_2Na \cdot 2C_6H_5 \cdot CO_2H$ , which crystallises in silky needles.

W. G.

**Hydrogen Persulphides. VI. Trisulphides and Tetrasulphides of certain Carboxylic Acids.** IGNAZ BLOCH and MAX BERGMANN (*Ber.*, 1920, 53, [B], 961-977. Compare A., 1911, i, 46, and previous abstracts).—Acyl disulphides may be readily prepared by the action of the requisite acid chloride on hydrogen disulphide in the presence of a small quantity of zinc chloride. In the case of fatty and fatty-aromatic acid chlorides, the trisulphides may be obtained in a similar manner, but with aromatic acid chlorides there is a marked tendency towards the shortening of the sulphur chain, with the production of disulphides, and this occurs to such an extent as to enable the crude hydrogen polysulphide to be advantageously used in the preparation of the latter. The aromatic trisulphides are readily prepared from sulphur dichloride and the potassium salt of the requisite thioacid ( $2C_6H_5 \cdot CO \cdot SK + SCl_2 \rightarrow 2KCl + S_3Bz_2$ ), and an extension of this method to sulphur monochloride affords a means of obtaining the tetrasulphides.

The acyl persulphides are, in general, colourless or faintly coloured crystalline substances, which are rather more stable than the hydrogen persulphides, but which, particularly in the cases of the higher sulphides, gradually decompose when preserved. The disulphides have already been extensively investigated; the reactions of the higher sulphides are closely similar to those of the disulphides, the additional sulphur which they contain being generally separated in the elementary state. The tri- and tetrasulphides show a marked tendency to eliminate sulphur and pass into the disulphides, and this action is particularly noticeable in the presence of feebly basic substances, which do not cause too extensive decomposition. Thus benzoyl tetrasulphide could be

degraded step by step by means of dimethylaniline, and benzoyl trisulphide was identified as the primary product of the change.

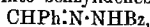
*Acetyl trisulphide*,  $S_3Ac_2$ , forms a greenish-yellow, viscous oil.  $D_4^{20}$  1.3423, which becomes colourless at  $-20^\circ$ , and can be frozen to a crystalline mass, leaflets or needles, m. p.  $-19^\circ$  to  $-17^\circ$ . It could not be prepared in the pure condition. *Phenylacetyl trisulphide*, colourless, six-sided plates, has m. p.  $85-86^\circ$  after slight previous softening, and, with phenylhydrazine yields sulphur, hydrogen sulphide, and the phenylhydrazide of phenylacetic acid, m. p.  $172-173^\circ$ . Phenylacetyl disulphide, prepared from phenylacetyl chloride and hydrogen disulphide, has m. p.  $60-61^\circ$  (compare Johnson, A., 1906, i, 954). *Benzoyl trisulphide* forms prisms, m. p.  $167-168^\circ$  (corr.), but when crystallised from indifferent solvents is obtained in six-sided plates, which soften and partly melt at about  $90^\circ$ , resolidify, and again melt at  $122-123^\circ$  (corr.). The phenomenon appears to depend on polymorphism; conversion of the form of lower into that of higher melting point can be effected by crystallisation from mixtures of chloroform or carbon disulphide and light petroleum in the presence of sulphur chloride, whilst the reverse change is effected by the use of indifferent solvents. *Benzoyl tetrasulphide* forms almost colourless, flat prisms or broad leaflets, m. p.  $83-84^\circ$ , after very slight previous softening; it is converted by potassium thiobenzoate into benzoyl trisulphide, and, ultimately, benzoyl disulphide. *Anisoyl disulphide*, prepared from potassium thioanisate and oxidising agents or from crude hydrogen persulphide and anisoyl chloride in the presence of zinc chloride, crystallises in needles, m. p.  $121-122^\circ$  (corr.), and resembles benzoyl disulphide closely in its properties (the isolation of *potassium thioanisate* and of *thioanisic acid*,  $OMe \cdot C_6H_4 \cdot CO \cdot SH$ , small, colourless needles, m. p.  $82-83^\circ$ , is described). *Anisoyl tetrasulphide* forms faintly coloured, microscopic needles, m. p.  $104-105^\circ$  (corr.), after slight softening. *Anisoyl trisulphide* closely resembles the benzoyl compound; when crystallised from chloroform in the presence of sulphur chloride, it has m. p.  $168-169^\circ$  (corr.), but, when obtained in the absence of the latter, the melting point is lower and very indefinite, marked softening usually occurring below  $110^\circ$ , and complete liquefaction between  $150^\circ$  and  $160^\circ$ .

H. W.

#### The Action of Benzoyl Chloride on Potassium Sulphide.

MAX BERGMANN (*Ber.*, 1920, 53, [B], 979-984).—The action of molar proportions of potassium sulphide and benzoyl chloride in alcoholic solution is stated to lead to the formation of potassium thiolbenzoate,  $Ph \cdot COSK$ , which is converted by a second molar proportion of benzoyl chloride into benzoyl sulphide. The reaction is found to follow a much more complex course when the sulphide and chloride are initially present in the molecular ratio, 1:2; benzoyl sulphide is only obtained in small amount, whilst the main products are benzoyl disulphide and a substance which can readily be separated from the latter by reason of its greater stability towards alcoholic ammonia and is regarded as *benzylidene*

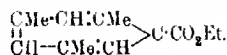
*bisthiobenzoate*,  $\text{CHPh}(\text{S}\cdot\text{COPh})_2$ ; it forms characteristic, moss-like masses of needles or prisms, m. p.  $141^\circ$  (corr.), and is readily decomposed by alcoholic alkali, but is stable to 1% alcoholic hydrogen chloride. The presence of the benzylidene group is proved by its conversion by hydrazine into benzylidenebenzoylhydrazine,



m. p.  $207\text{--}208^\circ$  (corr.). Benzylidene bisthiobenzoate can also be prepared by the action of dry hydrogen chloride on a mixture of benzaldehyde and thiobenzoic acid, or, less advantageously, from benzylidene chloride and potassium thiobenzoate (2 mols.) in alcoholic solution. Benzylidene bisthiobenzoate reacts with piperidine in alcoholic solution to yield *N*-thiobenzooylpiperidine,  $\text{C}_5\text{H}_9\text{N}\cdot\text{C}_6\text{H}_4\text{S}\cdot\text{COPh}$ , pale yellow plates, m. p.  $63\text{--}64^\circ$ , b. p. ca.  $205^\circ/12$  mm. *Ausylidene bisthiobenzoate* forms prisms, m. p.  $79\text{--}80^\circ$ , to a cloudy liquid which becomes transparent at  $81^\circ$ ; it does not appear to yield *N*-thiobenzooylpiperidine with piperidine. H. W.

**Preparation of Chlorylsulphonamides.** MAX CLAAS (D.R.P. 318899; from *Chem. Zentr.*, 1920, iv, 14—15).—The sulphonamides of aromatic carboxylic acids are converted into the corresponding dichloryl compounds in the usual manner. The introduction of the carbonyl group into the nucleus increases the stability of the chlorylsulphonamides. *Dichlorylsulphonamidobenzoic acid*, from *p*-sulphonamidobenzoic acid and alkali hypochlorite solution and subsequent addition of acetic acid, has m. p.  $203^\circ$ . Sulphuric acid precipitates small amounts of *monochlorylsulphonamidobenzoic acid*, m. p.  $223^\circ$ , from the filtrate. H. W.

**The Action of Diazoacetic Ester on Mesitylene.** EDUARD BECHNER and KARL SCHOTTENHAMMER (*Ber.*, 1920, 53, [B], 865—873).—Previous investigations (A., 1911, i, 50, and earlier abstracts) have shown that aromatic hydrocarbons condense with ethyl diazoacetate with loss of nitrogen and formation of carboxylic esters of norcarane, and that the latter are transformed at elevated temperatures into derivatives of cycloheptatriene. The primary addition appears to occur in such a manner that a quaternary carbon atom is never formed; the case of mesitylene, therefore, is of peculiar interest, since such a grouping must of necessity be present in the initial compound, if actually formed. It is found, however, that the product of the change is *ethyl trimethylcycloheptatrienecarboxylate*, which probably has the constitution



The action between mesitylene and ethyl diazoacetate is best carried out at  $135\text{--}140^\circ$ ; the crude product, when distilled, gives a fraction, b. p.  $137\text{--}143^\circ/12$  mm., which consists of ethyl trimethylcycloheptatrienecarboxylate mixed with ethyl fumarate. At  $115\text{--}120^\circ$ , reaction proceeds very slowly, but ultimately yields the same products; in the presence of copper powder, a brisk action

occurs, which leads almost exclusively to the formation of ethyl fumarate. *Trimethylcycloheptatrienecarboxylic acid*, m. p.  $142^{\circ}$ , is obtained by hydrolysis of the crude ester mixture, and is converted by the successive action of phosphorus pentachloride and ammonia into the corresponding *amide*, long, colourless needles, m. p.  $151^{\circ}$ . The acid unites readily with bromine, but the additive product is unstable and easily loses hydrogen bromide.

The first fractions obtained during the distillation of the crude ester give, when hydrolysed, a mixture of trimethylcycloheptatrienecarboxylic acid and mesitylacetic acid, m. p.  $168^{\circ}$ . The ester of the latter acid is also obtained by the protracted heating of ethyl trimethylcycloheptatrienecarboxylate at  $200^{\circ}$ , whilst the acid itself is formed when trimethylcycloheptanetricarboxylic acid is treated with glacial acetic acid and hydrogen bromide at the ordinary temperature. The action of bromine on mesitylacetic acid or trimethylcycloheptanetricarboxylic acid in warm glacial acetic acid solution yields *αα*-dibromomesitylacetic acid,  $C_6H_2Me_3 \cdot CBr_2 \cdot CO_2H$ , m. p.  $249.5^{\circ}$ .

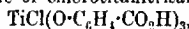
In similar condensations, the formation of derivatives of  $\beta$ -phenylpropionic acid in small quantity has invariably been observed; this appears to be the case in the present instance also, since the action of alcoholic ammonia on the ester very slowly leads to the formation of mesitylacetamide and an *amide*, m. p.  $118^{\circ}$ , which, when hydrolysed, yields an *acid*, m. p.  $46.5^{\circ}$ , probably  $\beta$ :3:5-dimethylphenylpropionic acid; it could not be obtained in quantity sufficient for an extended investigation.

Trimethylcycloheptatrienetricarboxylic acid absorbs six atoms of hydrogen in glacial acetic acid solution in the presence of platinum and gives the oily *trimethylcycloheptanetricarboxylic acid*, which is stable towards permanganate, and is characterised by conversion into the corresponding *amide*, long needles, m. p.  $148^{\circ}$ . H. W.

**Melting Point of Salicylic Acid.** W. J. BUSH & Co., LTD. (*Perfumery and Essent. Oil Rec.*, 1920, 11, 207).—Pure salicylic acid melts at  $159^{\circ}$ , and m. p. of  $158^{\circ}$  to  $159^{\circ}$  are regularly obtained with commercial samples of British salicylic acid. The m. p.  $156$ – $157^{\circ}$ , quoted in the pharmacopœia and commonly accepted, is consequently considerably too low. G. F. M.

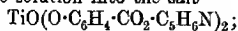
**Molecular Compounds of Inorganic Haloids. VII. Hydroxycarboxylic Acid Titanates, Polyphenol Titanates, and certain Allied Compounds.** ARTHUR ROSENHEIM and OTTO KAR SORGE (*Ber.*, 1920, 53, [B], 932–939).—A further extension of previous work (compare A., 1915, i, 537, and previous abstracts).

*Titanitrisalicylic acid*,  $C_6H_4 \begin{smallmatrix} \diagup O \diagdown \\ CO_2 \end{smallmatrix} Ti(O \cdot C_6H_4 \cdot CO_2H)_2$ , is obtained when the hydrochloride of chlorotitanitrisalicylic acid,



is exposed to the air; the *pyridinium*, *ammonium*, *sodium*, and *potassium* salts are described.

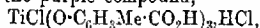
Titanidisalicylate,  $\text{Ti}\left(\begin{smallmatrix} \text{O} \cdot \text{C}_6\text{H}_4 \\ \text{O} \cdot \text{CO} \end{smallmatrix}\right)_2$  (*loc. cit.*), is converted by pyridine in alcoholic solution into the salt



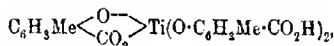
the corresponding ammonium and mercuric salts have been investigated.

Titanium chloride reacts with a solution of phenyl salicylate in anhydrous ether to yield the compound  $[\text{Ti}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Ph})_3]_2\text{TiCl}_6$ ; with salicylamide, under the same conditions, a brown, smeary mass is obtained, which evolves hydrogen chloride and gives  $[\text{TiCl}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2)_3]_2\text{HCl}$ ; an alcoholic solution of the latter deposits the compound  $\text{TiCl}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2)_3 \cdot \text{EtOH}$ .

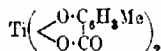
The behaviour of *m*-cresotic acid closely resembles that of salicylic acid. Thus, the purple compound,



passes, on exposure to air, into the yellowish-white acid,



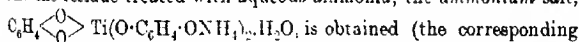
the pyridinium and ammonium salts of which are described. The acid is converted by heat into titanium basic *m*-cresotate,



which is transformed by alcohol and pyridine into the yellow salt,  $\text{TiO}(\text{O} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO}_2 \cdot \text{C}_5\text{H}_5\text{N})_2$ ; the corresponding ammonium and potassium salts are described.

Other hydroxycarboxylic acids appear to react in an analogous manner with titanium chloride; the salts derived from protocatechuic, gallic, and pyrogallolcarboxylic acids were, however, too soluble to permit their isolation in the pure state.

In the compounds which have been described so far, the hydroxyl group is, from the point of view of the co-ordination theory, equivalent to the carboxyl group. It is, therefore, not surprising to find that the polyphenols yield complexes with titanium tetrachloride. Thus, when ethereal solutions of catechol and titanium chloride are mixed, a vigorous action occurs, the primary product of which could not be isolated; if, however, the ether is removed and the residue treated with aqueous ammonia, the ammonium salt,



is obtained (the corresponding potassium and silver salts are described). Other chlorides behave similarly. Thus, silicon tetrachloride and catechol give colourless, very unstable crystals of *tricatechol silicon chloride* (?), which are converted by alcoholic ammonia into *ammonium tricatechol silicate*,  $\text{C}_6\text{H}_3\text{O}_3 \cdot \text{Si}(\text{O} \cdot \text{C}_6\text{H}_3 \cdot \text{ONH}_4)_2$ , and by alcoholic pyridine into the corresponding pyridinium salt. Similarly, zirconium oxychloride and thorium nitrate react with a boiling aqueous ammoniacal solution of catechol to yield the salts,  $\text{C}_6\text{H}_3\text{O}_3 \cdot \text{Zr}(\text{O} \cdot \text{C}_6\text{H}_3 \cdot \text{ONH}_4)_2 \cdot 7\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_3\text{O}_3 \cdot \text{Th}(\text{O} \cdot \text{C}_6\text{H}_3 \cdot \text{ONH}_4)_2 \cdot 7\text{H}_2\text{O}$ .

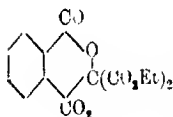


Titanium chloride reacts readily with pyrogallol in ethereal solution, and the product obtained after removal of the solvent is transformed by aqueous ammonia into the *salt*,  
 $\text{OH}\cdot\text{Ti}[\text{O}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{ONH}_4]_3\cdot 3\text{H}_2\text{O}.$

H. W.

**The Constitution of Phthalylmalonic Esters and Allied Substances.** JOHANNES SCHEIBER and GEORG HOPFER (*Ber.*, 1920, 53, [B], 898—913).—Recent spectrochemical observations (A., 1918, i, 436) have led Auwers and Auffenberg to cast doubts on the correctness of the formula,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\rangle\text{C}(\text{CO}_2\text{Et})_2$  (I), assigned to phthalylmalonic ester by Scheiber (A., 1912, i, 559), and to revert to the older formula,  $\text{CO}\langle\begin{smallmatrix} \text{H} \\ \text{O} \end{smallmatrix}\rangle\text{C}:\text{C}(\text{CO}_2\text{Et})_2$  (II). The problem has now been re-investigated by examining the action of ozone on the ester and a number of related compounds.

A substance of formula (II) would be expected to react with ozone to give an ozonide which would be decomposed by cold water with the formation of phthalic acid and ethyl mesoxalate; the accumulation of negative substituents around the double bond would not inhibit this reaction, since it is found that the similarly constituted benzylidenephthalide yields phthalic acid and benzaldehyde, whilst benzylidenemalononic acid gives benzaldehyde or benzoic acid and mesoxalic acid, and  $\alpha$ -cyanocinnamic ester yields benzaldehyde or benzoic acid and the semi-nitrile of mesoxalic ester (*phenylhydrazone*, silky leaflets, m. p. 181°). Actually, ethyl phthalylmalonate is only slowly attacked by ozone at  $-20^\circ$  and yields small amounts of phthalic acid and ethyl mesoxalate, but the main product (about 80%) is an oily substance (this occasionally solidifies to a colourless mass, m. p. about  $48^\circ$ , which cannot be further purified), which is characterised by its unusual stability towards water and appears to be a peroxide, probably having the annexed formula. Hydrolysis of the latter, in so far as it can be effected by water, leads to the production of phthalic acid and ethyl mesoxalate, and this doubtless accounts for a portion of these substances which are found after ozonisation of phthalylmalonic ester.



The results of the experiments, therefore, tend to confirm the symmetrical structure of the ester, and the apparent discordance between the authors' conclusions and those of Auwers and Auffenberg are ascribed to the dissimilarity of the experimental conditions and to the possibility of desmotropic change. It appears that the solid ester has the constitution (I), and, in the molten or dissolved state, passes more or less completely into the forms (II) or (III).  $\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}\cdot\text{CO}_2\text{Et}$   
 $\text{CO}-\text{O}-\text{C}\cdot\text{OEt}$ ; indications of the presence of the latter are yielded by the evolution of carbon dioxide during ozonisation.

Very similar observations are recorded with succinylmalonic ester, which, after ozonisation and treatment of the product with water, is found to give small quantities of succinic acid and ethyl mesoxalate, the main product, however, being a *diperoxide* characterised by great stability towards water. The solid ester, therefore, appears to have the symmetrical constitution and to undergo desmotropic change when melted or dissolved.

When similarly treated, the two ethyl phthalylacetoacetates yield phthalic acid, acetic acid, and ethyl glyoxylate, but whereas the ester of lower melting point gives the products in quantitative amount, that of higher melting point only gives them in 80% yield. The constitution of the former is without doubt expressed by the formula  $\text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}(\text{CO}_2\text{Et})_2$ , whilst the latter in all probability has

the constitution  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \text{COEt} \diagdown \\ \diagdown \text{COMe} \diagup \end{smallmatrix}$ ; in any case, the structure  $\text{CO} \begin{smallmatrix} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{O} \diagup \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \text{COMe} \diagdown \\ \diagdown \text{CO}_2\text{Et} \diagup \end{smallmatrix}$  is definitely excluded, since such a compound would yield phthalic acid and ethyl  $\alpha\beta$ -diketobutyrate, the latter of which is not produced.

The results of ozonisation do not completely confirm the constitutions previously ascribed to the phthalylbenzoylacetones; the smooth conversion of the isomeride of lower melting point into phthalic acid and phenyl methyl triketone indicates that it has the formula  $\text{CO} \begin{smallmatrix} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{O} \diagup \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \text{COMe} \diagdown \\ \diagdown \text{C}_6\text{H}_5 \diagup \end{smallmatrix}$ . The constitution of the isomeride of higher melting point has not been definitely elucidated, but the present investigation accentuates the improbability that the compounds are stereoisomerides.

Phthalylacetylacetone yields phthalic acid, methylglyoxal, and acetic acid, thus confirming the structure.  $\text{C} \begin{smallmatrix} \diagup \text{C}_6\text{H}_4 \cdot \text{CO} \diagdown \\ \diagdown \text{O} \diagup \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \text{COMe} \diagdown \\ \diagdown \text{COMe} \diagup \end{smallmatrix}$ , assigned to it previously.

H. W.

**[Formation of Iron Tannates.]** C. A. MITCHELL (*Analyst*, 1920, 45, 254—256).—When solutions of ferrous salts and gallotannic acid are mixed, a pale ferrous tannate appears to be formed, any ferric salt present being immediately reduced to the ferrous condition. When this solution of ferrous tannate is exposed to the air, it is slowly oxidised, and yields insoluble incrustations and deposits. The earlier precipitates contain a proportion of iron (for example 5.38—5.75%) corresponding with Wittstein's iron tannate,  $\text{Fe}_2(\text{C}_{14}\text{H}_9\text{O}_9)_6$  (*Jahresber. Chem.*, 1848, 28, 221). As the oxidation proceeds, the successive deposits contain more iron, and finally approximate in composition to the precipitate which Pelouze (*Ann. Chim. Phys.*, 1833, [ii], 54, 337) obtained by exposing a solution of ferric sulphate and gallotannic acid to the air for a month, namely,  $\text{C}_{14}\text{H}_9\text{O}_9 \cdot \text{Fe} \cdot \text{Fe} \begin{smallmatrix} \diagup \text{C}_{14}\text{H}_9\text{O}_9 \diagdown \\ \diagdown \text{C}_{14}\text{H}_9\text{O}_9 \diagup \end{smallmatrix}$ , which contains 8.4% of iron. This compound, however, is not formed at

first from ferric sulphate, but the presence of ferric salts in the solution promotes the oxidation to the more highly oxidised compounds. The addition of a small amount of hydrogen peroxide to a solution of ferrous tannate causes the precipitation of a tannate containing iron, corresponding with the amount (14.21%)

in Wittstein's tannate,  $\text{C}_{14}\text{H}_9\text{O}_9 \cdot \text{Fe} \cdot \text{Fe} \cdot \text{C}_{14}\text{H}_9\text{O}_9$ . If a large amount of hydrogen peroxide is added, a heavy precipitate containing 21 to 24% of iron is immediately formed. This approximates in composition to Ruoss's basic tannate,  $(\text{C}_{14}\text{H}_7\text{O}_9)_2(\text{FeO})_2$ , with 24.42% of iron (*Zeitsch. anal. Chem.*, 1902, **41**, 732). Neither of these compounds, however, appears to be formed in the atmospheric oxidation of ferrous tannate. By adding a few drops of pine oil to a ferrous tannate solution, a dense precipitate containing about 8.1% of iron is obtained. A similar catalytic acceleration of the oxidation to Pelouze's tannate is effected by the addition of saliva, but in this case the action proceeds much more slowly.

C. A. M.

**Manufacture of Hydroxyaldehydes and their Ethers.** ANDRE WEISS (Brit. Pat. 139153).—Aromatic hydroxyaldehydes or their ethers are obtained by the interaction of a phenol or phenol ether with formaldehyde and an aromatic nitroso-compound, such as nitrosobenzene, *p*-nitrosodimethylaniline, etc. For example, vanillin is obtained in excellent yield by heating for several hours on a water-bath a mixture of guaiacol (1 mol.), formaldehyde (1 mol.), and *p*-nitrosodimethylaniline ( $\frac{1}{2}$  mol.), methyl or ethyl alcohol being added as a diluent, and hydrogen chloride being bubbled through continuously. *p*-Aminodimethylaniline is formed as a by-product, and is removed by extraction with benzene or ether after rendering alkaline with sodium hydroxide and distilling off the alcohol. The liquor is then acidified and the vanillin extracted with benzene and purified by distillation in a vacuum.

G. F. M.

**Influence of Substitution in the Components on the Equilibria in Binary Solutions. XXVI. The Binary Systems of Acetophenone and Benzophenone, respectively, with Phenols and their Derivatives.** ROBERT KREMAN and HERMANN MARKL (*Monatsh.*, 1920, **41**, 43—75. Compare this vol., i, 564).—Freezing-point curves have been constructed for the binary systems, acetophenone with  $\alpha$ -naphthol,  $\beta$ -naphthol, catechol, quinol, resorcinol, pyrogallol, phenol, *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol, 2:4-dinitrophenol, and picric acid respectively, and for benzophenone with picric acid and 2:4-dinitrophenol. It is shown that both  $\alpha$ -naphthol and  $\beta$ -naphthol form an equimolecular compound with acetophenone, melting at 13° and 8° respectively. The three dihydroxybenzenes each form an equimolecular compound with acetophenone, which melts as follows: quinol, 40°; resorcinol, 13°; catechol, 1°. Pyrogallol forms two compounds with acetophenone, one molecule of aceto-

phenone combining with one half and one molecule of pyrogallol respectively, and the compounds melting at 18.5° and 21°. It is shown that the equimolecular compound with catechol is very much more dissociated in the fused mass than that with resorcinol. Benzophenone forms no compounds with any of the substances used; here simple eutectics are formed, as follows: at 35°, with 20% of 2:4-dinitrophenol, and at 27° with 29% of picric acid. Acetophenone forms no compounds with the nitrophenols or with 2:4-dinitrophenol; here, again, simple eutectics are formed as follows: at 2.5°, with 47% of *o*-nitrophenol; at -16°, with 41.5% of *m*-nitrophenol; at -4°, with 38% of *p*-nitrophenol; at 12°, with 21% of 2:4-dinitrophenol. In the case of picric acid, an equimolecular compound between acetophenone and picric acid, and a further compound between two molecules of acetophenone and one molecule of picric acid, m. p. 50°, are formed. J. F. S.

**Asymmetric Synthesis.** RICHARD WEISS (*Monatsh.*, 1919, **40**, 391-402).—The interaction of phenyl-*p*-tolylketen and *l*-menthol in absolute ethereal solution yields *l*-menthyl *d*-phenyl-*p*-tolylacetate. This reaction represents an asymmetric synthesis, since an optically active compound is formed from an optically inactive one without the intermediate formation of the racemic compound. According to the author's results, the *l*-menthyl *d*-phenyl-*p*-tolylacetate described by McKenzie and Widdows (*T.*, 1905, **107**, 702) was partly racemised.

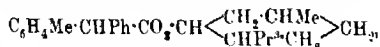
*Dibromobenzyl p-tolyl ketone*,  $\text{CBr}_2\text{Ph}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises in yellow prisms, m. p. 127.5-128°, and yields *p*-toluic acid when fused with potassium hydroxide. When heated with alcohol in a sealed tube at 140-160°, it gives:

4-Methylbenzil,  $\text{COPh}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$ , which forms crystals, m. p. 99-101°, and distils unchanged in a vacuum. Since the action of hydrazine on an alcoholic solution of 4-methylbenzil yields only a small proportion of a crystalline substance, together with much syrupy material incapable of purification, the preparation of the phenyl-*p*-tolylketen was carried out by way of phenyl-*p*-tolylglycolic acid.

*Phenyl-p-tolylglycolic acid*,  $\text{OH}\cdot\text{CPh}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CO}_2\text{H}$ , prepared by heating 4-methylbenzil with potassium hydroxide solution at 150-160°, forms crystals, m. p. 131-133°, and is coloured blood-red by concentrated sulphuric acid.

$\alpha$ -Chlorophenyl-*p*-tolylacetyl chloride,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CPhCl}\cdot\text{COCl}$ , prepared by the method used by Staudinger for  $\alpha$ -chlorodiphenylacetyl chloride (*Annalen*, 1907, **356**, 72), forms a yellow oil, which is decomposed with moderate rapidity by atmospheric moisture.

*l*-Menthyl *d*-phenyl-*p*-tolylacetate,



prepared by reducing  $\alpha$ -chlorophenyl-*p*-tolylacetyl chloride with zinc turnings under ether and in an atmosphere of carbon dioxide, and treating the phenyl-*p*-tolylketen thus formed with *l*-menthol.

forms a yellow, viscous oil, b. p. 190—196°/1 mm.,  $[\alpha]_D$  in acetone —45.40°. The ester is accompanied by a small proportion of phenyl-*p*-tolylacetic acid, due to the action of water on the keten.

The phenylacetic acid used for the synthesis of the benzyl *p*-tolyl ketone was prepared by converting benzyl chloride into benzyl cyanide and hydrolysing the latter, and was found to be mixed with a little *phenylacetobenzylamide*,  $\text{CH}_3\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ , which may also be obtained by the Schotten-Baumann reaction from benzylamine and phenylacetyl chloride, and forms crystals, m. p. 122°. This compound is formed in accordance with the following scheme:  $\text{CH}_3\text{Ph}\cdot\text{CN} + \text{CH}_2\text{PhCl} \rightarrow \text{CH}_3\text{Ph}\cdot\text{CClN}\cdot\text{CH}_2\text{Ph} \rightarrow \text{CH}_2\text{Ph}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{CH}_2\text{Ph} \rightarrow \text{CH}_3\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ .

T. H. P.

**The Action of an Alcoholic Solution of Potassium Hydroxide in the Presence of Zinc Powder on the Bromobenzophenones and on some of their Derivatives.** P. J. MONTAGNE (*Rec. trav. chim.*, 1920, **39**, 483—491).—Bromobenzophenones and their derivatives when boiled in an alcoholic solution of potassium hydroxide with zinc powder are reduced to benzhydrols, but, at the same time, the bromine is completely replaced by hydrogen, and a certain amount of resinous material is formed.

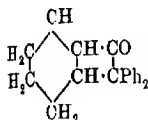
W. G.

**Ketens. XXXI. *cyclobutanedione* Derivatives and the Polymeric Ketens.** H. STAUDINGER (*Ber.*, 1920, **53**, [B], 1085—1092).—It has recently been suggested by Schroeter (A., 1917, i, 145) that the polymeric ketens are molecular compounds instead of *cyclobutane* derivatives, as postulated by Staudinger. The author does not agree with this view, and, in the present communication, gives a survey of the literature of this class of substances, in which it is shown that their properties can be adequately interpreted by the *cyclobutane* formulation. New experimental evidence is not brought forward.

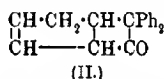
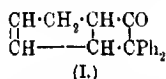
H. W.

**Ketens. XXXII. *cyclobutane* Derivatives from Diphenylketen and Ethylene Compounds.** H. STAUDINGER and E. SUTER [and, in part, R. FLATT, H. W. KLEVER, KARL KNOCH, and E. STANDT] (*Ber.*, 1920, **53**, [B], 1092—1105).—Diphenylketen readily condenses with styrene, yielding 1:1:3 *triphenylcyclobutane-2-one*,  $\text{CHPh}\cdot\text{CH}_2$ , colourless needles, m. p. 135—136°, from which the initial products are regenerated by heating at about 200°. The substance could not be caused to yield an oxime, semicarbazone, or phenylhydrazone, nor did it condense with benzaldehyde in the presence of alkali. When treated with methyl-alcoholic sodium hydroxide solution, it gives *αγ-triphenyl- $\alpha$ -butyric acid*, white powder, m. p. 178—179° (*methyl ester*, m. p. 125—126°), which is converted at 260° into styrene and diphenylacetic acid. Similarly, diphenylketen and *p*-methylstyrene give 1:1-diphenyl-3-*p*-tolyl-*cyclobutane-2-one*, colourless needles, m. p. 117°, which is decomposed into its constituents by heat, and with alkali gives

*aa-diphenyl-γ-p-tolyl-n-butyric acid*, white powder, m. p. 207°. *p-Chlorostyrene*, b. p. ca. 74°/12 mm., is prepared by the action of magnesium methyl iodide on *p*-chlorobenzaldehyde and subsequent dehydration of the carbinol so formed by heating it with potassium pyrosulphate; the yields are poor (30%), on account of the readiness with which polymerisation occurs. With diphenylketen, the substance yields 1:1-diphenyl-3-*p*-chlorophenylcyclobutane-2-one, crystalline powder, m. p. 120–121°, from which *aa-diphenyl-γ-p-chlorophenyl-n-butyric acid*, m. p. 178–179°, is obtained in the usual manner. Similarly, 1:1-diphenyl-3-*p*-anisylcyclobutane-2-one, m. p. 77–78°, is prepared from *p*-methoxystyrene. Vinyl ethyl ether unites with diphenylketen to form 1:1-diphenyl-3-ethoxycyclobutane-2-one, crystalline powder, m. p. 71–72°, which is relatively unstable and decomposes into its constituents when gently heated, and, apparently,



when preserved; it is converted by alcoholic alkali into an acid, m. p. about 116°. Tetrahydrobenzene and diphenylketen yield a substance (annexed formula), colourless needles, m. p. 129–130°, which is transformed by alkali into diphenylcyclohexylacetic acid, crystalline powder, m. p. 122°. cyclopentadiene and diphenylketen unite readily in molar proportions, giving the compound I or II, m. p. 89–90°, which is readily resolved by heat into

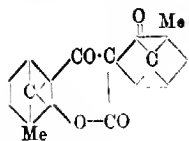


its components, and with alkali gives the corresponding acid, m. p. 125°. The substance is readily reduced to the corresponding saturated compound, colourless needles, m. p. 92°, which decomposes when heated into diphenylketen and cyclopentene. Diphenylketen unites similarly with phenylmethylfulvene to yield a product, m. p. 168–169°. Unlike the previous cases, *N*-methylpyrrole unites with two molecules of diphenylketen even when the substances are used in molar proportions; the product is a white, crystalline powder, m. p. ca. 206° (decomp.) after softening at 190°. Pyrrole itself yields *N*-diphenylacetylpyrrole, m. p. 122°. *aa*-Diphenylethylene gives 1:1:3:3:5:5-hexaphenylcyclohexane-2:4-dione, m. p. 180–181°, which yields *aaγγδδ*-hexaphenyl-δ-ketohexzoic acid, needles, m. p. 121–123°. H. W.

**Ketens. XXXIII. Attempts to Prepare Optically Active Ketens.** H. STAUDINGER and S. SCHOTZ (*Ber.*, 1920, 53, [E], 1105–1124).—The investigation was undertaken in the hope that the isolation of an optically active keten would greatly facilitate the investigation of the rate at which these substances unite with various compounds by allowing the course of the reaction to be followed polarimetrically. The present communication describes the efforts to obtain certain camphorketens. Unfortunately, the

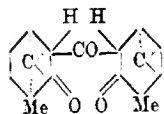
substances are too unstable to permit their isolation in the unimolecular form, but various dimerides have been obtained and characterised as *cyclobutane* derivatives. The fact that in certain instances stereoisomerides can be isolated is further evidence against Schroeter's conception of the substances as additive products.

Camphorcarboxylic chloride is most conveniently prepared by the action of thionyl chloride at the ordinary temperature on the



corresponding acid. When heated, it loses hydrogen chloride rapidly at 170°, slowly, but with the production of a purer product, at 100°, and passes into the pyronone derivative (annexed formula), needles, m. p. 196°,  $[\alpha]_D + 293.8^\circ$  in benzene, +302.2° in ethyl acetate solution, which is identical with the product obtained by

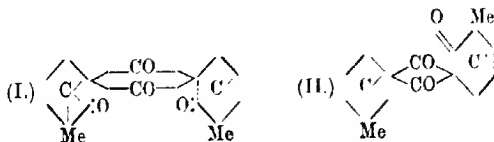
Kachler and Spitzer by the action of acetyl chloride on camphorcarboxylic acid. Attempts to depolymerise the substance were unsuccessful. When subjected to the prolonged action of concentrated hydrochloric acid at the ordinary temperature, the dimeride is transformed into the corresponding hydroxy-acid, m. p. 262° (Kachler and Spitzer give m. p. 264°), which, when heated at about 290°/0.1 mm., is reconverted into the substance, m. p. 196°, a little camphor being simultaneously formed. The acid is very sensitive towards alkali, and is converted by aqueous potassium hydroxide into the *ketone* (annexed formula), m. p. 180°.



Attempts were made to prepare camphorketen from bromocamphorcarboxyl bromide (the latter, m. p. 80–81°, is obtained by the action of bromine in the presence of carbon

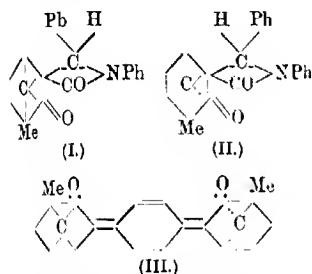
disulphide on camphorcarboxyl chloride, removal of the halogen acids from the solution by carbon dioxide, and subsequent treatment of the solution with hydrogen bromide); the bromide reacts readily with zinc in ethereal solution, but yields only the acid, m. p. 264°, and the pyronone compound, m. p. 196° (see above).

Camphorcarboxyl chloride readily loses hydrogen chloride under the influence of basic reagents, particularly quinoline, and the resultant solution contains *camphorketen* in the free state for a short period. Polymerisation, however, readily results, with the formation of a mixture of *cis*- and *trans*-*dicamphorcyclobutanediones* (I and II); the former has m. p. 152–153°,  $[\alpha]_D + 116.3^\circ$  in benzene.



+126.8° in ethyl acetate solution, whilst the latter has m. p. 150–151°,  $[\alpha]_D + 61.1^\circ$  in benzene, +62.9° in ethyl acetate. When

either polymeride is heated for a short time at 160—170°, the keten is transitorily formed, which rapidly passes into the pure product of m. p. 196°. With *p*-toluidine, either substance gives camphor-carboxyl-*p*-toluidide, whilst with hydrochloric acid the same acid is obtained as from the pyronone derivative; with methyl alcohol and alkali, methyl camphorcarboxylate, b. p. 143—145°/12 mm., 142°/13 mm.,  $[\alpha]_D + 57.91^\circ$  in ethyl acetate solution, is obtained. With ethyl-alcoholic potassium hydroxide solution, the reaction follows a different course, yielding small amounts of a new acid, m. p. about 187°, but neither camphorcarboxylic acid nor its ethyl ether; the main product is dicamphorketone, m. p. 182° (see above),



which is more conveniently prepared by the action of dilute aqueous sodium hydroxide on an ethereal solution of either polymeride.

The formation of camphorketen from the cyclobutanedione derivative is established, not only by the appearance of coloration, but also by addition of certain reagents, which combine so rapidly with the keten that combination

occurs before polymerisation can take place. Thus, for example, the dicamphorcyclobutanediones readily react with benzylidene-aniline to yield the two stereoisomeric  $\beta$ -lactams (I and II), m. p.'s 166.5° and 195—196° respectively, and with *p*-benzoquinone to give dicamphorquinodimethane (III), orange-coloured crystals, m. p. 305—306°.

H. W.

**The Chloroquinones.** A. J. DEN HOLLANDER (*Rec. trav. chim.*, 1920, **39**, 481—482).—The author has repeated the work of Peratoner and Genco (A., 1895, i, 342) and of Oliveri Tortorici (A., 1898, i, 303) on the preparation of 2:3-dichloro-*p*-benzoquinone. He found no evidence of the formation of this compound, the products he obtained being 2:5-dichloro-*p*-benzoquinone and 2:6-dichloro-*p*-benzoquinone.

W. G.

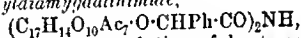
**The Fission of certain Glucosides and Amygdalin.** GÉZA ZEMPLÉN (*Ber.*, 1920, **53**, [B], 996—1006).—Amygdalin is known to contain a biose which is hydrolysed by acids or by emulsin to two molecules of dextrose, but its identity has not been further established. The experiments now described were undertaken in the hope that hepta-acetylamygdalin might undergo fission under the influence of a solution of hydrogen bromide in glacial acetic acid in such a manner as to yield phenylbromoacetone and the acetyl compound of the biose of amygdalin. The feasibility of this plan is shown by experiments with a number of acetylated



cellobiosides, but, unfortunately, the process proves not to be available for amygdalin, in which the presence of the cyanogen group renders the glucosidic union between mandelic acid and the biose more stable than the ethereal bond between the two glucose residues. Attempts to avoid this difficulty by using hepta-acetyl-amygdalinic acid were unsuccessful, and it was further not found possible to obtain a suitable crystalline derivative of amygdalin which was free from nitrogen.

*Hepta-acetylbenzylcellobioside*,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{C}_{12}\text{H}_{14}\text{O}_{10}\text{Ac}_7$ , long, colourless, silky needles, m. p.  $193^\circ$  after softening at  $190^\circ$ ,  $[\alpha]_D^{20} - 37.4^\circ$  in chloroform solution, is prepared by the interaction of acetyl bromocellobiose and benzyl alcohol in benzene solution in the presence of silver carbonate, and is hydrolysed by hydrogen bromide in glacial acetic acid to acetyl bromocellobiose, m. p. about  $190^\circ$  (decomp.),  $[\alpha]_D^{20} + 92.0^\circ$  in chloroform solution. Under similar conditions, the latter substance was also obtained from *hepta-acetylmethylcellobioside*, small, colourless needles, m. p.  $180^\circ$ , from *hepta-acetylisobutylcellobioside*, slender, colourless needles, m. p.  $196-197^\circ$ ,  $[\alpha]_D^{20} - 21.5^\circ$  in chloroform solution, and from *hepta-acetylphenylcellobioside*, yellowish-grey needles, m. p.  $193^\circ$  (prepared from phenol and acetyl bromocellobiose in the presence of quinoline). Tetra-acetyl- $\beta$ -methylglucoside appeared to undergo fission in a similar manner, since, although acetyl bromoglucose could not be isolated in the crystalline state, its presence could be deduced from the abundant formation of phenylglucosazone after hydrolysis of the product with calcium carbonate and subsequently with aqueous alcoholic alkali. On the other hand, tetra-acetylsalicin yielded *tetra-acetylsalicin bromide*,  $\text{CH}_2\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_7\text{O}_4\text{Ac}_4$ , long, colourless prisms, m. p.  $167^\circ$ ,  $[\alpha]_D^{20} + 47.1^\circ$  in chloroform solution, the free hydroxyl groups of the saligenin residue being replaced by bromine.

*Tetradeca-acetyldiamygdalinimide*,



is prepared by saturating a solution of hepta-acetylamygdalin in chloroform containing a little absolute alcohol with dry hydrogen chloride; it forms long needles, m. p.  $212^\circ$ ,  $[\alpha]_D^{20} - 72.1^\circ$  in chloroform solution. It is hydrolysed by alcoholic potassium hydroxide solution to *diamygdalinimide*, which is hydrolysed by boiling aqueous hydrochloric acid with abundant production of dextrose.

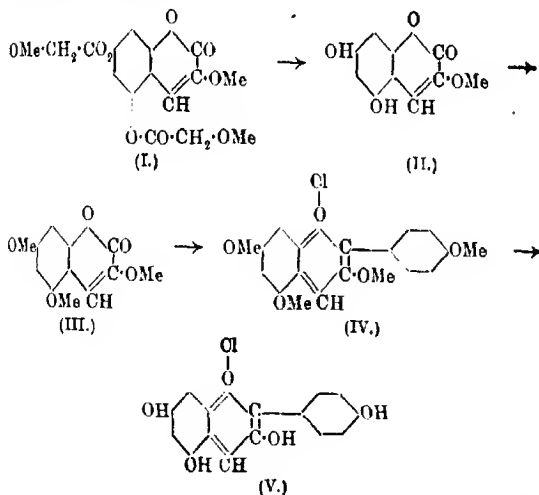
H. W.

**Action of Light on Colloidal Chlorophyll in the Presence of Stabilising Agents.** RENE WURMSER (*Compt. rend. Soc. Biol.*, 1920, **83**, 437-438; from *Chem. Zentr.*, 1920, i, 895).—Colloidal chlorophyll, prepared according to the directions of Willstätter and Stoll, is much more sensitive to light than the natural product. This sensitiveness can be greatly depressed by certain colloids, of which gelatin appears to be the most potent; white of egg and gum arabic are much less powerful, whilst starch is inactive. Possibly an action of salts on the complex may be observed in plants. If the effect of the protective colloid is due to shielding

from oxygen, the same effect may possibly be expected from carbon dioxide.

H. W.

**Synthesis of Pelargonidine.** RICHARD WILLSTÄTTER and LÁSZLÓ ZECHMEISTER (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, **34**, 886—893).—The condensation of 2:4:6-trihydroxybenzaldehyde with sodium methoxyacetate and methoxyacetic anhydride at 150—155° gives 5:7-dimethoxyacetyl-3-methoxycoumarin (I), prisms, m. p. 170—171° (corr.), from which, by treatment with cold dilute sodium hydroxide solution, 5:7-dihydroxy-3-methoxycoumarin (II), prisms or rhombic leaflets, m. p. 280—285° (corr.; decomp.), is obtained. 3:5:7-Trimethoxycoumarin (III), prisms or oblong leaflets, m. p. 171—172° (corr.), formed from the latter by treatment with diazomethane, reacts with excess of magnesium anisyl bromide, the product giving 3:5:7-trimethoxy-2-p-anisylpyrylium chloride (IV), bluish-red prisms (compare Decker and Fellenberg, A., 1907, i, 1064), from which the methyl groups are removed by means of boiling hydriodic acid in presence of phenol. 3:5:7-Trihydroxy-2-p-hydroxyphenylpyrylium iodide thus obtained gives a corresponding chloride (V), identical in composition, crystalline form, solubility, reaction, and absorption spectrum with the chloride of natural pelargonidine (Willstätter and Bolton, A., 1914, i, 564; 1915, i, 283).

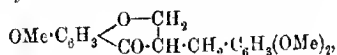


J. K.

**Chromanones. II. The Brazilin and Hæmatoxylin**  
 Question. P. FRIEßER and H. J. EMMER (*Ber.*, 1920, **53**, [B], 945—953).—A further contribution to the synthesis of substances

allied to brazilin and hæmatoxylin (compare Pfeiffer and Grimmer, A., 1917, i, 661).

7-Methoxychromanone [7-methoxy-2:3-dihydro- $\gamma$ -benzopyrone] condenses with vanillin methyl ether in alcoholic solution in the presence of sodium hydroxide to yield 7:3':4'-trimethoxy-3-benzylidene-2:3-dihydro- $\gamma$ -benzopyrone, almost colourless needles, m. p. 139—140°, which is reduced by hydrogen in the presence of platinum black to 7:3':4'-trimethoxybenzylchroman [7:3':4'-trimethoxy-3-benzyl-2:3-dihydro- $\gamma$ -benzopyrone],



colourless, shining needles, m. p. 87°. Similarly, 7-methoxychromanone condenses with piperonal to give the *piperonylidene* derivative, pale yellow, felted needles, m. p. 149°, and with furfuraldehyde to yield the *furfurylidene* compound, needles, m. p. 119—120°.

7:8-Dimethoxychromanone [7:8-dimethoxy-2:3-dihydro- $\gamma$ -benzopyrone], colourless leaflets, m. p. 100—101°, is obtained by the reduction of the corresponding chromone with hydrogen in the presence of platinum black; it yields a *semicarbazone*, colourless needles, m. p. 218° (decomp.), an *oxime*, long, shining needles, m. p. 152°, a *piperonylidene* derivative, small, pale yellow needles, m. p. 181°, and a *furfurylidene* compound, pale yellow needles, m. p. 133°. Attempts to condense the chromanone with vanillin methyl ether met with difficulty, but a *substance*, slender, yellow needles, m. p. 133—134°, which is probably 7:8:3':4'-tetramethoxy-3-benzylidene-2:3-dihydro- $\gamma$ -benzopyrone, was isolated in amount too small for identification.

Gallacetophenone dimethyl ether condenses with piperonal in the presence of alcohol and warm 50% aqueous sodium hydroxide solution yielding *piperonylidene*gallacetophenone dimethyl ether,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_3\text{O}_2\cdot\text{CH}_2$ , deep yellow needles, m. p. 178° (*perchlorate*, dark violet crystals; *acetyl* derivative, yellow leaflets, m. p. 127°), and with furfuraldehyde to give *furfurylidene*gallacetophenone dimethyl ether, golden-yellow needles or leaflets, m. p. 105° (*acetyl* derivative, m. p. 92°). H. W.

**Tannins. IV. Hamameli-tannin. II.** KARL FREUDENBERG and DANIEL PETERS (*Ber.*, 1910, 53, [B], 953—961).—Further investigation has confirmed the previous conclusion (A., 1919, i, 215) that hamameli-tannin is an ester-like compound of gallic acid (2 molecules) and a sugar related to the hexoses. The identification of the latter has not yet been accomplished, but it appears to consist of an almost pure aldo-hexose. It does not give the reactions of a pentose. On the other hand, it differs from the usual hexoses in that it cannot be converted into lævulinic acid, but its action towards magenta-sulphurous acid and Fehling's solution indicates that it is a true sugar.

Considerable improvements have been effected in experimental

technique. The hydrolysis is effected by tannase (the preparation of which is described in detail), and the process only goes to completion with solutions containing less than 2.5% of the tannin. The course of the action can be followed for the greater part by polarimetric observations or, preferably, by measurement of the gradual increase of the acidity of the solution. The use of lead carbonate and basic lead acetate for the removal of residual gallic acid has been found to be disadvantageous, since the susceptible hamamelis-sugar is thereby extensively changed, and these reagents are now replaced by the washed clay of H. Wislicenus, which is found to adsorb gallic acid and tannin from the cold solution without affecting the sugar. An improved method of purifying hamamelis-tannin is fully described. H. W.

**Physical Properties of some Alkaloids.** H. ZEEHUISEN (*Arch. Exp. Path. Pharm.*, 1920, **86**, 342-372).—Some physical properties, such as odour, solubility, surface tension, electrical charge, according to Zwaardemaker's method, etc., of forty-two alkaloids were studied. The results are tabulated together with some of the properties of these alkaloids previously established.

S. S. Z.

**Complex Metallic Ammines. III. Dichlorotetrapyridine-cobalt Salts.** THOMAS SLATER PRICE (T., 1920, **117**, 860-865).

**Quinoline-2-, -3-, and -4-sulphonic Acids.** E. BESTHORN and BERTHA GEISSELBNECHT (*Ber.*, 1920, **53**, [B], 1017-1033).—An investigation has been made of the quinoline-2-, -3-, and -4-sulphonic acids which is of particular interest, since quinolines sulphonated in the pyridine nucleus do not appear to have been described previously. In general, the sulphonic acids are well-crystallised substances, the melting points of which are above 270° and have not been determined. They are fairly strong, monobasic acids. The alkali salts are freely soluble in water, as are also the alkaline-earth compounds, although certain of the latter could be obtained in the crystalline condition. The 2-acids are so unstable that they lose sulphur dioxide when their aqueous solutions are boiled, and neither from them nor from the 4-acids was it found possible to prepare the corresponding sulphonyl chlorides or sulphonamides, on account of the readiness with which sulphur dioxide is eliminated. The 3-acids, on the other hand, exhibit a much more normal behaviour.

*Quinoline-2-sulphonic acid*, slender, colourless needles, is prepared by the oxidation of 2-thiolquinoline with nitric acid (D 1.4) or by the action of boiling aqueous sodium sulphite solution on 2-chloroquinoline. The *silver* salt is described. Similarly, 4-chloroquinoline and sodium sulphite yielded *quinoline-4-sulphonic acid*, colourless needles, the *calcium* salt (+4H<sub>2</sub>O) and *silver* salt of which were analysed. *4-Methylquinoline-2-sulphonic acid*, obtained by the oxidation of 2-thiol-4-methylquinoline or from sodium sulphite and 2-chloro-4-methylquinoline, forms slender,

colourless needles, which give 2-hydroxy-4-methylquinoline when boiled with water; the sodium and calcium salts are described. 2-Methylquinoline-4-sulphonic acid is prepared from 4-thiol-2-methylquinoline or 4-chloro-2-methylquinoline; the potassium, sodium, ammonium, calcium, and silver salts were investigated.

For the preparation of the 3-sulphonic acids other methods were necessary, since 3-thiolquinoline is unknown, and attempts to prepare 3-thiol-2-methylquinoline from 3-hydroxy-2-methylquinoline were unsuccessful; in addition, the stability of the halogen atom in 3-chloro-2-methylquinoline is such as to render reaction of the substance with sodium sulphite impracticable. The authors have therefore used a method of the Höchst Farbwerke, according to which *o*-aminobenzaldehyde is condensed with sodium acetone-sulphonate in aqueous alkaline solution, and have thus obtained 2-methylquinoline-3-sulphonic acid (the barium and silver salts, the sulphonyl chloride, pale yellow needles, m. p. 121°, and the sulphonamide, m. p. 227°, are described). Potassium 2-methylquinoline-3-sulphonate is converted by benzaldehyde and zinc chloride at 180° into 2-styrylquinoline-3-sulphonic acid, which is remarkably stable to acid oxidising agents, but is readily oxidised by potassium permanganate in alkaline solution to a mixture of 2-carboxyquinoline-3-sulphonic acid and 2-aldehydoquinoline-3-sulphonic acid,  $C_{10}H_7O_5NS \cdot H_2O$  (the oxime, colourless needles, and phenylhydrazone [!]) are described); the aldehyde remains unchanged when boiled with fuming nitric acid or with dilute sulphuric acid and chromic acid, but, on the other hand, a boiling aqueous solution of the calcium salt is readily oxidised by silver oxide to the calcium salt of 2-carboxyquinoline-3-sulphonic acid,  $C_{10}H_5O_5NSCa \cdot 4H_2O$  (the calcium hydrogen salt is also described). The ready solubility of the free acid in water, combined with the paucity of material, prevented the acid itself from being isolated. The crude acid, however, is converted by concentrated hydrochloric acid at 170° into quinoline-3-sulphonic acid, long, colourless, slender needles ( $+nH_2O$ ); the barium salt forms colourless, hydrated needles. H. W.

**Allyl 2-Phenylquinoline-4-carboxylate.** A. GAMS (U.S. Pat. 1336952).—Allyl 2-phenylquinoline-4-carboxylate, long needles, m. p. 30°, b. p. 260°/15 mm., forms a hydrochloride, small, citron-yellow needles, m. p. 145–147°, which is instantly hydrolysed by water. The ester is tasteless, and the hydrochloride has a slight sweet taste. The ester can be made by the usual methods, and has therapeutic properties similar to those of the alkyl esters of 2-phenylquinoline-4-carboxylic acid. CHEMICAL ABSTRACTS.

**Influence of Substitution in the Components on the Equilibria in Binary Solutions. XXV. The Binary Systems of Carbazole and Phenols.** ROBERT KREMAN and FERDINAND SLOVAK (*Monatsh.*, 1920, 41, 23–42. Compare following abstract).—Freezing-point curves have been constructed for the

systems carbazole with  $\alpha$ -naphthol,  $\beta$ -naphthol, catechol, resorcinol, quinol, pyrogallol, the three nitrophenols, 2:4-dinitrophenol, and picric acid respectively. It is shown that the two naphthols, pyrogallol, and the three dihydroxybenzenes do not form compounds with carbazole; in all these cases simple eutectics are formed, as follows:  $\alpha$ -naphthol,  $90.0^\circ$  with 7% of carbazole;  $\beta$ -naphthol,  $115.0^\circ$  with 9.0% of carbazole; catechol,  $102.0^\circ$  with 4.0% of carbazole; resorcinol,  $107.0^\circ$  with 7.0% of carbazole; quinol,  $163.6^\circ$  with 15% of carbazole; pyrogallol,  $126.0^\circ$  with 1% of carbazole. Similar relationships are found for the nitrophenols and 2:4-dinitrophenol, simple eutectics only being formed, as follows: o-nitrophenol,  $43.5^\circ$  with 3.0% of carbazole; m-nitrophenol,  $92.0^\circ$  with 5.0% of carbazole; p-nitrophenol,  $106.7^\circ$  with 6.0% of carbazole; and 2:4-dinitrophenol,  $98.6^\circ$  with 17.0% of carbazole. Picric acid forms an equimolecular compound with carbazole, m. p.  $183^\circ$ , and this compound forms an eutectic with carbazole at  $181.5^\circ$  containing 51% of carbazole, and with picric acid at  $113^\circ$  containing 5% of carbazole.

J. F. S.

**Influence of Substitution in the Components on the Equilibria in Binary Solutions. XXIV. The Binary System Acridine with Phenols.** ROBERT KREMANN and FERDINAND SLOVAK (*Monatsh.*, 1920, **41**, 5—21. Compare this vol., i, 570, and preceding abstract).—Freezing point curves have been constructed for the binary systems of acridine with phenol,  $\alpha$ -naphthol,  $\beta$ -naphthol, quinol, catechol, and resorcinol respectively. It is shown that, in the case of phenol and acridine, two compounds are formed, namely, between two molecules of phenol and one molecule of acridine, m. p.  $87^\circ$ , and between two molecules of phenol and three molecules of acridine, m. p.  $101^\circ$ . In the case of  $\beta$ -naphthol, two compounds are also formed, between three molecules of  $\beta$ -naphthol and two molecules of acridine, m. p.  $135^\circ$ , and between one molecule of  $\beta$ -naphthol and two molecules of acridine, m. p.  $96^\circ$ . Acridine and  $\alpha$ -naphthol also form two compounds, an equimolecular compound, m. p.  $115.5^\circ$ , and a compound between one molecule of  $\alpha$ -naphthol and two molecules of acridine, m. p.  $97^\circ$ . Quinol and resorcinol each form a single compound with acridine of the composition, two molecules of acridine with one molecule of the phenol; these compounds have melting points  $209.5^\circ$  and  $179.5^\circ$  respectively. In the case of catechol, a single compound is also formed, but this is an equimolecular compound, m. p.  $144.5^\circ$ . The affinity of phenol,  $\beta$ -naphthol, and  $\alpha$ -naphthol for acridine increases in the order named.

J. F. S.

**Preparation of p-Nitrophenylcarbamide Chloride.** FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 319969, additional to D.R.-P. 241822; from *Chem. Zentr.*, 1920, ii, 777).—p-Nitroaniline is added to a solution of carbonyl chloride in an indifferent solvent, and, if necessary, is further treated with the chloride until the amine hydrochloride has completely disappeared;

temperatures may be employed which are considerably above that at which dry *p*-nitrophenylcarbamide chloride is transformed into the corresponding carbimide. It is preferable first to dissolve the carbonyl chloride, in part or completely, in the solvent, such as nitrobenzene, benzene, or carbon tetrachloride, and then to add the amine.

H. W.

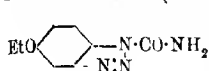
**Alteration in Taste of the Sweetening Agent, Dulcin [*p*-Phenethylcarbamide] as a Result of Chemical Change.**  
H. THOMS and K. NETTESHEIM (*Ber. deut. pharm. Ges.*, 1920, 30, 227—250).—It is found that *p*-phenethylcarbamide,



loses its sweetening power when a considerable variety of acidic or basic substituents is introduced into the benzene nucleus.

The only *p*-phenethylcarbamide substituted in the nucleus which has been described previously is that obtained by Berlinerblau by the action of nitric fumes on an alcoholic solution of dulcin; this compound is now shown to be 3-nitro-*p*-phenethylcarbamide, since it is identical with the product obtained by the successive action of carbonyl chloride and ammonia on 3-nitro-*p*-phenetidine. (3-Nitrophenetidine hydrochloride is obtained as by-product of this action. It commences to dissociate at 130°, and action is complete at 150°. It is extremely readily hydrolysed by water, and the change in colour from the yellow salt to the cinnabar-red base may be conveniently employed in testing for traces of moisture.) 3-Nitro-*p*-phenethylcarbamide may also be obtained by the action of dilute nitric acid on dulcin at the ordinary temperature. (The readiness with which dulcin is converted into its intensely yellow nitro-derivative forms the basis of a convenient and rapid method of distinguishing between dulcin and other sweetening agents.) 2-Nitro-*p*-phenetidine is similarly transformed by carbonyl chloride and ammonia into 2-nitro-*p*-phenethylcarbamide, long, yellow, shining needles, m. p. 178.5° after softening at 176°. This substance is also obtained by the action of a cold mixture of nitric acid (53%) and concentrated sulphuric acid on dulcin, but the yield is only 60%, as a considerable amount of the latter is destroyed. It cannot be conveniently prepared from 2-nitro-*p*-phenetidine hydrochloride and potassium cyanate in boiling aqueous solution, since the main product of this action is dinitro-*p*-diphenethylcarbamide,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4[\text{NO}_2])\cdot\text{OEt}$ , yellow needles, m. p. 201°. 3-Nitroso-*p*-phenethylcarbamide is conveniently prepared by the addition of the requisite quantity of sodium nitrite solution to a suspension of finely powdered dulcin in much concentrated hydrochloric acid; it forms pale yellow needles, which decompose at 51—52°. 3-Amino-*p*-phenethylcarbamide, needles, decomposing at 179°, is prepared by the reduction of the corresponding nitro-compound with tin and hydrochloric acid; the hydrochloride, colourless leaflets, decomposing slowly at 170°, the sulphate, prisms, and the acetyl derivative, coarse, colourless needles, m. p. 181°, are described. When the salts are treated with nitrous acid, the

diazonium compound is produced, which rapidly passes into the azimino-derivative (annexed formula), slender needles, m. p. about



141° (decomp.) after softening at 138°. Similarly, 2-nitro-*p*-phenethylcarbamide is reduced by tin and hydrochloric acid to 2-amino-*p*-phenethylcarbamide, colourless needles, m. p. 202° (the hydrochloride [ $+ \text{H}_2\text{O}$ ] and acetyl derivative, slender, silky needles, m. p. 217–218°, are described). Nitrous acid converts the substance into a dark brown dye. *p*-Phenethylcarbamide-2-sulphonic acid is prepared by the action of fuming sulphuric acid on dulcin at 50–60°; the sparingly soluble lead and the sodium salt were analysed. The constitution of the compound is proved by its formation from a boiling aqueous solution of carbamide nitrate and *p*-phenetidine-2-sulphonic acid. It could not be transformed into the corresponding phenol by fusion with potassium hydroxide. 2-Chloro-*p*-phenethylcarbamide, small, matted needles, m. p. 148°, is obtained in almost quantitative yield from 2-chloro-*p*-phenetidine hydrochloride and potassium cyanate. The similarly prepared 2-bromo-*p*-phenethylcarbamide forms long prisms, m. p. 156°. A dichloro-*p*-phenethylcarbamide, needles, m. p. 200°, is obtained from dichloro-*p*-phenetidine by the successive action of carbonyl chloride and ammonia.

H. W.

#### The Sweetening Power of Derivatives of *p*-Hydroxyphenylcarbamide.

F. BOGAECKER and R. ROSENBRUCH (*Ber. deut. pharm. Ges.*, 1920, **30**, 251–258).—The authors have attempted to obtain a sweetening agent analogous to dulcin (*p*-phenethylcarbamide), but possessing greater sweetening power and greater solubility in water, and have therefore prepared hydroxy-*p*-ethoxyphenylcarbamide,  $\text{HO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , and  $\beta$ -y-dihydroxy-*p*-propoxyphenylcarbamide,  $\text{HO} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ . An improvement in the solubility in water is noticed in either case, but the former compound is less sweet than dulcin and has a bitter after-taste, whilst the latter is not sweet.

*Hydroxy-*p*-ethoxyphenylcarbamide*, plates, m. p. 160°, is obtained by the action of ethylene chlorohydrin on *p*-hydroxyphenylcarbamide in the presence of sodium ethoxide or, alternatively, by condensing ethylenechlorohydrin with *p*-nitrophenol to *p*-nitrophenyl hydroxyethyl ether, pale yellow needles, m. p. 94–95°, and reducing the latter with zinc dust and hydrochloric acid to *p*-amino-phenyl hydroxyethyl ether hydrochloride, needles, m. p. 204–205°, and converting the amino-ether into the corresponding carbamide by an aqueous solution of calcium cyanate.  $\beta$ -*Dihydroxy-*p*-propoxyphenylcarbamide*, needles, m. p. 156–157°, is prepared from *p*-hydroxyphenylcarbamide and a monochlorohydrin.

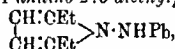
*p*-Hydroxyphenylcarbamide reacts with chloroacetamide at 100–110° in the presence of sodium methoxide, yielding *p*-carbamidophenoxyacetamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , small leaflets, m. p. 264° after previous softening; it is tasteless.

H. W.



**The Iodoamidines.** J. BOUGAULT and P. ROBIN (*Compt. rend.*, 1920, 171, 38—40).—Benzamidine reacts with iodine in the presence of dilute aqueous sodium hydroxide to give *iodobenzamidine*, m. p. 117°, which is apparently a derivative of hypoiodous acid. It reacts with potassium iodide in the presence of hydrochloric acid, the whole of its iodine being liberated, thus showing that the iodine is linked directly with the nitrogen and is not a substituent of the benzene ring. Anisamidine and piperonamidine give similar crystalline iodoamidines. W. G.

**Action of Substituted Hydrazines on the Acyclic  $\alpha\beta$ -Diketones.** E. E. BLAISE (*Compt. rend.*, 1920, 171, 34—36).—Whilst hydrazine gives with acyclic  $\alpha\beta$ -diketones a mixture of derivatives of pyridazine and tetrahydropyridazine, the substituted hydrazines give pyrrole derivatives. Thus *s*-dipropionylethane gives with phenylhydrazine 1-anilino-2:5-diethylpyrrole,



m. p. 65.5°. Similarly, with phenylmethylhydrazine, it yields 1-methylanilino-2:5-diethylpyrrole, b. p. 162°/16 mm., which, when reduced with zinc and hydrochloric acid in acetic acid solution, gives aniline and 2:5-diethylpyrroline, b. p. 154°/760 mm. or 62°/28 mm., giving a *platinichloride*, m. p. 180° (decomp.); an *aurichloride*, m. p. 100—101°, and a *picrate*, m. p. 97—98°. Dipropionylethane reacts with ammonia to give 2:5-diethylpyrrole, b. p. 100°/29 mm., giving an *oxime*, m. p. 155°. On reduction, the pyrrole gives the 2:5-diethylpyrroline described above. W. G.

**Coloured Sensitisers Derived from Quinolines, Quinaldines, and Lepidines containing Dimethylamino- and Diethylamino-groups.** H. BARBIER (*Bull. Soc. chim.*, 1920, [iv], 27, 427—439).—6-Dimethylaminoquinoline gives an *ethiodide*, m. p. 212°, and an impure *isomeride*, m. p. 170°, in which the ethyl iodide is probably attached to the nitrogen of the  $\cdot\text{NMe}_2$  group.

When *p*-phenylenediethyldiamine, glycerol, sulphuric acid, and nitrobenzene are boiled together for three hours, 6-diethylaminoquinoline, b. p. 192—193°/20 mm., is obtained, giving a *hydrochloride*, a *platinichloride*, m. p. 280°, a *picrate*, m. p. 196°, a *methiodide*, m. p. 148°, and an *ethiodide*, m. p. 159°.

By the action of paraldehyde on *p*-phenylenedimethyldiamine in hydrochloric acid solution, 6-dimethylamino-2-methylquinoline, m. p. 101°, b. p. 319°/760 mm., is obtained, yielding a *hydrochloride*, a *sulphate*, a *platinichloride*, m. p. 199° (decomp.), a *mercurichloride*, m. p. 202°, two isomeric *methiodides*, m. p. 230° and 190° respectively, and two *ethiodides*, m. p. 226° and 100° respectively, of which the less fusible compound has the alkyl iodide attached to the ring nitrogen, whilst in the more fusible compound it is united to the alkylamino-nitrogen. Dimethylaminomethyl-quinoline also gives a *di-ethiodide*.

By the action of a mixture of acetone and formaldehyde saturated with hydrogen chloride on *p*-phenylenedimethyldiamine in hydrochloric acid, 6-dimethylamino-4-methylquinoline, m. p. 71°,

b. p. 330°, is obtained, giving a *hydrochloride*, a *platinichloride*, m. p. 200°, a *mercurichloride*, m. p. 206°, a *methiodide*, and probably two *ethiodides*.

The alkyl iodides of quinoline, and of 2- and 4-methylquinolines containing a dialkylamino-group, give a series of new colouring matters when condensed either among themselves or with alkyl iodides of other bases. Thus, 6-dimethylaminoquinoline ethiodide yields a cyanine when condensed with 2:6-dimethylquinoline ethiodide. In a similar way, the author has prepared cyanines by condensing the following mixtures: (b) 6-Dimethylaminoquinoline ethiodide and 6-dimethylamino-2-methylquinoline ethiodide. (c) 6-Diethylaminoquinoline ethiodide and 2:6-dimethylquinoline ethiodide. (d) 2:6-Dimethylquinoline ethiodide and 6-dimethylamino-2-methylquinoline ethiodide. (e) 6-Dimethylaminoquinoline methiodide and 2:6-dimethylquinoline methiodide. (f) 2:6-Dimethylquinoline methiodide and 6-dimethylaminoquinoline amyl iodide. (g) 6-Dimethylaminoquinoline ethiodide and 2:6-dimethylquinoline methiodide. (h) 6-Dimethylaminoquinoline methiodide and 2:6-dimethylquinoline ethiodide. (i) 6-Dimethylaminoquinoline methiodide and 6-dimethylamino-2-methylquinoline methiodide. (j) 6-Dimethylaminoquinoline ethiodide and 4-methylquinoline ethiodide. (k) 6-Dimethylaminoquinoline ethiodide and 6-dimethylamino-4-methylquinoline ethiodide. (l) 6-Dimethylamino-2-methylquinoline methiodide by itself. (m) 6-Dimethylamino-2-methylquinoline ethiodide by itself. (n) 6-Dimethylamino-4-methylquinoline by itself. (o) Dimethylaminoquinoline ethiodide, 2:6-dimethylquinoline ethiodide and formaldehyde. (p) Dimethylaminoquinoline ethiodide, dimethylamino-2-methylquinoline ethiodide and formaldehyde. (q) Dimethylamino-2-methylquinoline ethiodide by itself in the presence of formaldehyde. (r) *p*-Dimethylaminobenzaldehyde in turn with dimethylamino-2-methylquinoline methiodide and ethiodide, and dimethylamino-4-methylquinoline methiodide and ethiodide.

All these cyanines containing the active auxochrome group,  $\text{NMe}_2$  or  $\text{NEt}_2$ , are of interest in photography as sensitisers.

W. G.

**Condensation of 1-Phenyl-3-methyl-5-pyrazolone with Aldehydes and Ketones.** S. C. CHATTERJEE and B. N. GHOSH (*Proc. Asiatic Soc. Bengal*, 1919, 15, cxxxii—cxxxiii).—When 1-phenyl-3-methyl-5-pyrazolone is heated with aldehydes in molecular proportions, condensation usually takes place with the elimination of water. The compounds thus obtained have the general

formula  $\text{CHR}:\text{C} \begin{smallmatrix} \text{CO}-\text{NPh} \\ \text{CMe}_2\text{N} \end{smallmatrix}$ . These substances contain the chromophore  $\text{CO}:\text{C}:\text{C}$ , and are highly coloured. The present paper describes how aldehydes may be made to unite with pyrazolone, without the elimination of water, to form the intermediate additive hydroxyl compounds,  $\text{OH}:\text{CHR}:\text{CH} \begin{smallmatrix} \text{CO}-\text{NPh} \\ \text{CMe}_2\text{N} \end{smallmatrix}$ . The chromo-

phoric group,  $\cdot\text{CO}\cdot\text{C}\cdot\text{C}$ , is absent in them, and necessarily they are either colourless, or at any rate much less coloured than the corresponding unsaturated compounds. An attempt to synthesise pyranol derivatives from the pyrazolone and *o*-hydroxy-aldehydes is also described. Some new condensation products with aldehydes and ketones have been prepared, and in this connexion it has been pointed out that the aliphatic ketones are much less reactive than those of the aromatic series.

CHEMICAL ABSTRACTS.

**Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XXIII. The Binary System Antipyrine-Benzoic Acid.** ROBERT KREMANN and HERMANN MARRTL (*Monatsh.*, 1920, 41, 1—4. Compare A., 1919, ii, 458).—Freezing-point curves of the binary mixture benzoic acid and antipyrine have been made, from which it is seen that these two substances form a single equimolecular compound, m. p.  $66^{\circ}$ ; this compound forms an eutectic with benzoic acid at  $59.5^{\circ}$  containing 50.5% of antipyrine, and one with antipyrine containing 63.5% antipyrine at  $59.5^{\circ}$ . These results show that compounds such as salipyrine are due to combination of the carboxyl group with the antipyrine, and not to the phenolic group, for although phenol does form an equimolecular compound with antipyrine, it is a much weaker compound than that formed in the present experiments.

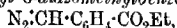
J. F. S.

**Condensation of Benzoin with Diamines.** S. C. CHATTERJEE and B. N. GHOSH (*Proc. Asiatic Soc. Bengal*, 1919, 15, cxxxi—cxxxi).—With the object of preparing substituted naphthadipyrindines or pyridinonaphthapyrroles, the reaction between benzoin and some of the naphthylenediamines has been studied, using the corresponding amine hydrochlorides as condensing agents. The reaction took place in the manner desired only in the case of 1:4- and 1:5-diamines, a mol. of the diamine combining with 2 mols. of benzoin with the elimination of 4 mols. of water. There are three possible formulae for each of these substances, and, although no conclusive proof is available, on the strength of indirect evidence it has been suggested that each of the two nitrogen atoms in both these substances forms part of a six-membered ring. Contrary to expectation, the 1:2-diamine yielded a product which appears to be identical with Fischer's diphenyldihydronaphthaquinoxaline (A., 1893, i, 284). Incidentally, the reaction between benzoin and benzidine was also studied, but in this case the closing of the ring did not take place, the compound obtained having the structure  $\text{C}_{12}\text{H}_4(\text{NH}\cdot\text{CHPh}\cdot\text{COPh})_2$ . An attempt was made to close the ring by boiling with acetic anhydride, but this only resulted in the formation of a diacetyl derivative.

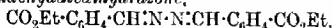
CHEMICAL ABSTRACTS.

**The Constitution of Yellow Sulphide Dyes.** JATINDRA KUMAR MAZUMDER and EDWIN ROY WATSON (T., 1920, 117, 830—834).

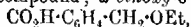
**Decomposition of Nitroso-compounds. II.** WILLIAM A. NOYES and JAMES A. COSS (*J. Amer. Chem. Soc.*, 1920, **42**, 1280—1286. Compare Oppé, A., 1913, i, 534).—When an ice-cold alcoholic solution of nitrosophthalimidine is treated with alcoholic sodium hydroxide, *ethyl o-diazomethylbenzoate*,



red crystals, m. p.  $39^\circ$ , separate, but at the ordinary temperature after two to three days, or on warming, nitrogen is evolved, and *ethyl phthalaldehydatedihydrazone*,



yellow crystals, m. p.  $145^\circ$ , is produced; this compound is decomposed by hydrochloric acid at  $130^\circ$  into phthalazone and phthalaldehydic acid. *Ethyl o-ethoxy-o-toluate*,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OEt}$ , an oil,  $D_{25}^{25}$  1.059,  $n_D^{25}$  1.49556, is produced by boiling an alcoholic solution of the diazo-compound; *o-ethoxy-o-toluic acid*,



melts at  $84.5^\circ$ . Similarly, the product of the action of sodium hydroxide on nitrosoaminolauronic anhydride (Noyes and Taveau, A., 1904, i, 807) is the dihydrazone of camphononic acid, which gives camphononic acid on hydrolysis, accompanied by *ethoxylauronic acid*,  $\text{OEt}\cdot\text{C}_8\text{H}_{17}\cdot\text{CO}_2\text{Et}$ , b. p.  $113\text{--}115^\circ/3$  mm. J. K.

**The Behaviour of Albumins and Antitoxins towards the Electric Current and the Isolation of Pure Antitoxic Albumin from Diphtheria Serum by the Electro-osmotic Method.** W. G. RUPPEL (*Ber. dent. pharm. Ges.*, 1920, **30**, 314—328).—If the blood serum of a normal animal is subjected to the action of an electric current in a cell which is divided into three partitions by suitable semipermeable membranes, and is so arranged that the middle cell contains the serum whilst the outer ones contain pure water in which the electrodes are placed, the fission of the electrolytes and wandering of the ions is first observed, whilst also a number of organic substances, such as amino-acids and degradation products of the albumins, are removed. As soon as the isoelectric point has been reached, the separation of euglobulin commences in the middle cell, and the reaction of the serum passes from neutral or faintly alkaline to acid. After removal of euglobulin, the separation of paraglobulin and albumins can be electrically effected, since the latter are more highly electrically charged, and therefore have a higher velocity of migration. The process can also be applied to the preparation of a pure antitoxic albumin, since it is found that the antitoxins are not in any way damaged or weakened by the electric current. In diphtheria serum, the antitoxin is mainly combined with the paraglobulin, whilst the euglobulin contains only small amounts of antitoxin, and the albumin practically none. The procedure has the advantage over precipitation methods that the usual inactive ingredients of the serum of immunised animals are also removed, whilst the danger of bacterial impurities can easily be avoided.

H. W.

**Tyrosine and the Dibasic Amino-acids in the Proteins of Yeast.** PIERRE THOMAS and ANDRÉ CHABAS (*Compt. rend.*, 1920, 170, 1622—1625).—An examination of the two proteins, cerevisin and zymocasein, previously found in yeast (compare A., 1913, i, 942, 1026), shows that cerevisin contains 4.13% of tyrosine, 6.26% of glutamic acid, and about 1% of aspartic acid. Zymocasein contains 2.85% of tyrosine, 0.94% of glutamic acid, and about 1% of aspartic acid. In the estimation of glutamic acid, the authors recommend the recrystallisation of its hydrochloride from 96% alcohol, in order to free it from ammonium chloride.

W. G.

**Hæmoglobins.** J. THONNARD (*Compt. rend. Soc. Biol.*, 1920, 83, 441—442; from *Chem. Zentr.*, 1920, i, 895).—In the reduction of oxyhæmoglobin with ammonium sulphide for distinguishing it from carbon monoxide hæmoglobin, the concentration of the reducing agent, the temperature, and the origin of the blood are of considerable importance. Experiments with human and animal blood are described. Under similar conditions, the oxyhæmoglobins of warm-blooded animals are much more stable than those of cold-blooded animals.

H. W.

**Carbon Monoxide Hæmoglobin.** J. THONNARD (*Compt. rend. Soc. Biol.*, 1920, 83, 443—444; from *Chem. Zentr.*, 1920, i, 895).—The times have been measured which, at different temperatures and with a uniform current of gas, are necessary for the conversion of carbon monoxide hæmoglobin by hydrogen into reduced hæmoglobin and by oxygen into oxyhæmoglobin, the experiments being performed with the blood of man, ox, and carp. The results show a complete parallelism between these actions and the stability of oxyhæmoglobin towards ammonium hydrogen sulphide (preceding abstract).

H. W.

**The Production and Properties of Pathological Melanin.** E. SALKOWSKI (*Arch. path. Anat.*, 1920, 227, 121—137).—Melanin was obtained from the intestinal tract and from tumours. A total of 995 grams of intestine yielded only 0.4406 gram of melanin, or 0.044%. In the preparation of melanin it is necessary to avoid heating with concentrated hydrochloric acid, since this may lead to the formation of melanoidin. The last traces of protein and fat can be removed by heating with glacial acetic acid. By this method, melanin is obtained in two fractions, one soluble in dilute sodium hydroxide, another insoluble even in 15% sodium hydroxide. By keeping, the soluble portion also tends to become insoluble. Melanin contains sulphur, which is firmly bound. It is resistant to oxidising agents, but is completely destroyed by permanganate in alkaline solution and by a mixture of potassium dichromate and sulphuric acid. Melanin consists in large measure of atom complexes belonging to the cyclic and heterocyclic series, but also contains aliphatic molecules.

CHEMICAL ABSTRACTS.

**Melanin and the Brown Endogenous Pigments.** B. BRAUN and MARTHA SCHMIDTMANN (*Arch. path. Anat.*, 1920, **227**, 137—152).—I. *Melanin*.—Melanin obtained from human tumours showed the following elementary analysis: C 51.92, H 5.21, N 11.03, S 3.42%. Melanoidin from horn contained: C 52.85, H 5.91, N 10.04, S 5.41%. Melanin is believed to be 3:4-dihydroxyphenylcysteine,  $C_6H_3(OH)_2 \cdot CH_2 \cdot C(SH)(NH_2) \cdot CO_2H$ .

II. *Endogenous pigment*.—The endogenous brown pigments are insoluble in ethyl alcohol and ether. The ability of these pigments to be stained with fat stains is due to extraneous material, and not to fatty acids contained within them. The pigment obtained from a heart showing brown atrophy was physically and chemically identical with melanin. III. *Relation of melanin to adrenaline*.—Melanin, like adrenaline, causes vasoconstriction. It does not cause hyperglycemia when injected intravenously. The action of adrenaline on the heart differs from that of melanin.

## CHEMICAL ABSTRACTS.

**Esterification of  $\alpha$ -Amino-acids.** H. A. SHONLE and H. H. MITCHELL (*J. Amer. Chem. Soc.*, 1920, **42**, 1265—1277).—The progress of esterification by the process of Osborne and Jones (A., 1910, i, 447) of individual amino-acids, and of mixtures obtained by the acid hydrolysis of casein, viginin, gelatin, and vegetable albumin, has been studied. The method depends on a determination of both the mineral and the unesterified amino-acids by the method of Sørensen (A., 1908, i, 115), and of the mineral acid alone by a Volhard estimation of chloride ion, allowance being also made for acidity due to addition of silver nitrate, when this has been used for purposes of decolorisation. This was, however, best accomplished by means of barium hydroxide and aluminium sulphate, which are preferable to sodium carbonate and potassium alum (Denis, A., 1911, ii, 163), because they can be quantitatively removed. Alanine can be esterified to the extent of 96%, lysine 82%, glutamic acid 85%, and a mixture of amino-acids 90%. Determination of the total amino acids after prolonged acid hydrolysis shows that a considerable proportion, 36% of those from casein, undergoes esterification during the removal of water from the crude acids preparatory to esterification by repeated evaporation with alcohol. Of the subsequent esterification, most occurred during the first hour, after which it progressed slowly until equilibrium was reached. There is no unesterifiable residue.

J. K.

**Mechanism of Enzyme Reaction.** EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 137—142).—A theoretical paper in which a number of hypotheses put forward to explain the mechanism of enzyme action are discussed.

J. F. S.

**The Influence of Hydrogen Ion Concentration on the Inactivation of Pepsin Solutions.** JOHN H. NORTHRUP (*J. gen. Physiol.*, 1920, **2**, 465—470).—Pepsin in solution at 38° is most

stable at a hydrogen-ion concentration of about  $P_H$  5.0, this point being independent of the anion of the acid used and of the purity of the enzyme solution. Increasing the hydrogen-ion concentration above  $P_H$  5.0 causes a slow increase in the rate of destruction of pepsin, whilst decreasing the hydrogen-ion concentration causes a very rapid increase in the rate of destruction of the enzyme.

The existence of an optimum range of hydrogen-ion concentration for the digestion of proteins by pepsin cannot be explained on the grounds of destruction of the enzyme by either too weak or too strong acid.

W. G.

**The Effect of the Concentration of Enzyme on the Rate of Digestion of Proteins by Pepsin.** JOHN H. NORTHROP (*J. gen. Physiol.*, 1920, 2, 471—498).—In certain cases, it is found that the rate of digestion of proteins by pepsin is not proportional to the total concentration of the pepsin, and it is suggested that this is due to the enzyme being in equilibrium with another substance, which the author, for convenience, calls peptone. This equilibrium is expressed by the law of mass action, according to the equation  $K = \text{concentration pepsin} \times \text{concentration peptone} / \text{concentration pepsin-peptone}$ , it being assumed that only the uncombined pepsin affects the hydrolysis of the protein. This was expressed as a differential equation, and was found to agree with experimental results. Pepsin inactivated by alkali enters the equilibrium to the same extent as active pepsin. Where the concentration of peptone is large with respect to that of the pepsin, that of the substrate being relatively constant, the equation simplifies to Schütz's rule,  $x = K \sqrt{TEA}$ , where  $x$  = amount of substrate digested,  $T$  = time,  $E$  = concentration of pepsin, and  $A$  = concentration of substrate.

An integral equation, identical with that of Arrhenius for the action of ammonia on ethyl acetate, is obtained, which holds for the entire course of the digestion, except for the first few minutes, with varying enzyme concentration.

It is shown that there are many analogies between the action of pepsin on albumin solutions and that of toxins on an organism.

W. G.

**Properties of a Specially Prepared Enzymic Extract, Polyzyme, and comparison of its Starch Liquefying Power with that of Malt Diastase.** JOKICHI TAKAMINE, jun., and KOKICHI OSHIMA (*J. Amer. Chem. Soc.*, 1920, 42, 1261—1265).—Polyzyme is an aqueous extract of diastatic enzymes, D 1.03—1.06, containing many other enzymes, made by a specially prepared culture of *Aspergillus oryzae* on media, consisting mainly of wheat bran. Its amylolytic power by Wohlgemuth's method is  $D_{30}^{60} 3.000$ ;  $D_{24}^{60} 115.000$ ; whilst Lintner's saccharogenic value at 21° is 43, and at 50°, 150. Its diastatic power remains unchanged at the ordinary temperature for six months, but is diminished after three hours above 40°. Its chemical composition is also given. J. K.

**Chemical Kinetics of Catalase. II. Catalase from a Germinated Bean: *Glycine hispida* maxim.** EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, 9, 59—73. Compare this vol., i, 194).—The enzyme from germinated beans, *Glycine hispida* maxim, was obtained as a dry, very active powder by digesting the crushed beans with distilled water saturated with toluene. The rate of decomposition of hydrogen peroxide by means of the catalase, *G. hispida* has been studied at 0°, 10°, 18°, and 25°, and it is found that the reaction follows the theory previously put forward for the catalase *Phyllostachys mitis*, Riv. (this vol., i, 453). There is a remarkable difference between the two kinds of enzyme. The temperature-coefficient of the rate of decomposition is  $\beta_k = 1.40$  for *P. mitis* and 1.85 for *G. hispida*. The difference observed is much too great to be attributed to the effects of the coexisting proteins. To test this point, the reaction was carried out with the enzyme containing different quantities of the coexisting soluble proteins, when no difference was found in the value of  $k'$ . It seems probable that catalase is a common name for a group of enzymes which have the power of catalysing hydrogen peroxide. These enzymes have different stabilities by which they may be recognised, and they probably have different physical properties. J. F. S.

**Chemical Kinetics of Catalase. III. Effect of Chemical Reagents on the Kinetics of Catalase.** EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, 9, 75—88. Compare preceding abstract).—The effect of adding small quantities of various substances to the reaction mixture of catalase and hydrogen peroxide has been studied at 0°. The experiments were carried out by adding to 18 c.c. of water 2 c.c. of a mixture of the catalase and the other chemical substance; this is kept at 0° for some time, usually about an hour, and then 4 c.c. of 0.1N-hydrogen peroxide is added. The rate of reaction is then measured in the usual way. The reactions are controlled by a similar procedure, but leaving out the foreign substance. The influence of the added substance is calculated from the equations,  $r_1 = kE_0/kE_{0(\text{control})}$ ;  $r_2 = k'/k'_{(\text{control})}$  in which  $kE_0$  and  $k'$  are the initial activity and decomposition constants in the presence of the added substance, and  $kE_{0(\text{control})}$  and  $k'_{(\text{control})}$  are the same values in the absence of the control;  $r_1$  and  $r_2$  are the coefficients of depressions of the activity. It is found that mercuric chloride, potassium cyanide, hydroxylamine, and phenylhydrazine entirely stop the reaction; strong oxidising agents such as potassium chlorate, potassium nitrate, and potassium dichromate retard the reaction very much; manganese sulphate increases the reaction, as also do soluble starch, glycine, and sucrose; dextrose is entirely without action. All other substances used retard the reaction; the order of the effect, starting with the greatest retardation, is aniline, silver sulphate, ferric alum, acetonitrile, ammonium molybdate, potassium dichromate, copper sulphate, yellow phosphorus (15 c.c. sat. sol.), chrome alum, potassium nitrate, mercuric cyanide, potassium chlorate, alanine, quinine, sodium



carbonate (*N*/100), brucine, sodium oleate, salicin, potassium chloride, asparagine, arsenious acid, menthol (15 c.c. sat. soln.), cobalt sulphate, urethane, ammonium vanadate, ammonium sulphate (*N*/1875), dextrose. The concentration used was *N*/1200, except where the contrary is stated. The effects of the electrolytes are attributed to oxidation, adsorption, or combination with the enzyme, and, as a secondary action, coagulation. J. F. S.

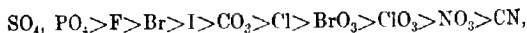
**Chemical Kinetics of Catalase. IV. Catalase from the Blood of Cattle.** EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, 9, 89—95. Compare preceding abstracts).—The reaction between catalase from the blood of cattle and hydrogen peroxide has been examined at 0°, 12·5°, 10°, 18°, and 25°. The reaction is similar in every respect to that observed with catalase from other sources. The temperature-coefficients are  $k=1\cdot23$  and  $k'=1\cdot63$ , which indicate that the present catalase differs from those previously examined.

Investigations with catalase from various sources show that the decomposition of the enzyme is approximately proportional to that of the hydrogen peroxide. When the enzyme is kept in the solid state for about a year, it is changed into a less active variety. The rate of reaction is expressed by  $-dC/dt=kEC$  and

$$(-dE/dt)/(-dC/dt)=k'/k.$$

The course of the reaction may be attributed to the fact that most of the labile kind of catalase had decomposed and that the chief rôle was taken by the stable variety. Similar behaviour was also found with solutions of the ferments which had previously been treated with hydrogen peroxide. This may also be attributed to the fact that the labile form decomposes more rapidly with hydrogen peroxide than the stable form. J. F. S.

**Action of Poisons on an Enzymatic Process. VI. Comparative Experiments on the Action of Certain Potassium and Sodium Compounds.** C. G. SANTESSON (*Skand. Arch. Physiol.*, 1920, 39, 236—256; from *Chem. Zentr.*, 1920, iii, 18—19).—The influence of a series of potassium and sodium salts on the ability of the catalase of frog's muscle to decompose hydrogen peroxide has been studied. In general, action of a salt depends on the anion rather than the cation. The anions may be approximately arranged in the following order:



in which the first member is least and the last most potent. The following series is established for the cations of a number of chlorides:  $\text{Mg} > \text{Zn} > \text{Ba} > \text{K} > \text{Sr} > \text{Ca} > \text{Na} > \text{Fe}$ . The order is not invariably maintained with different concentrations. H. W.

**Urease.** ARNOLD HAHN (*Ber. deut. pharm. Ges.*, 1920, 30, 329).—In their recent communication, Wester and Pin Yin Yi appear to

have completely overlooked the fact that certain of the results which they describe have been obtained previously by the author.

H. W.

**Chemical Kinetics of Urease.** EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, 9, 97—136).—The decomposition of urea by urease has been investigated under various conditions. The enzyme used was obtained from the soja bean by powdering the beans, extracting the powder with water saturated with toluene, filtering, and precipitating the filtrate with alcohol. The precipitate is washed with absolute alcohol and dried in a vacuum over calcium chloride. It is shown that when the reaction was examined in a faintly acid solution in the presence of a constant stream of carbon dioxide, the reactions  $\text{CO}(\text{NH}_2)_2 \rightarrow \text{NH}_2\text{CO}_2\text{NH}_4 \rightarrow (\text{NH}_4)_2\text{CO}_3$  take place with about the same velocity. Since the initial velocity  $[-dc/dt]_{t=0}$  is unaffected by any factor, the velocity constant  $k_1$  of the first reaction is determined by  $[-dC/dt]_{t=0}/C_0 = k_1$ , from which it is shown that  $k_1$  is proportional to the concentration of the urease, when the initial concentration of the urea is taken as constant. But it is a somewhat complicated function of the initial concentration of the urea, even though a constant quantity of urease is used at the start; the relationship is  $1/k_0(k_0 - k) = 8.2C_0^3$ , where  $k_0$  is the velocity constant for  $C_0 = 0.002$ ;  $k_0$  is taken as the standard because the effect of urea on urease can be reasonably neglected in such a dilute solution. The constant  $k$  of the second reaction seems to be independent of the initial concentration of urea, but it is approximately proportional to that of the urease. Although the ferment forms an heterogeneous system with the substrate, the reaction is homogeneous, that is, the decomposition of the substrate does not take place in the enzyme phase; at the same time, the rate of hydrolysis is not that with which the substrate diffuses into the enzyme phase, because the reaction is not affected by stirring. The mechanism of the reaction does not consist in the decomposition with a measurable velocity of an intermediate compound formed instantaneously by the reacting components, as is generally accepted. Further, the enzyme and the substrate do not form an intermediate compound with a measurable velocity, and the latter is not decomposed into the products of reaction and the enzyme as is assumed by van Slyke and Cullen. It is a simple catalytic action carried on in the substrate phase. The activity of the catalyst, however, is instantaneously diminished in an irreversible manner by the substrate, according to the equation given above. The experimental results are calculated by means of the formulae  $C_{M_1} = C_0 e^{-k_1 t}$ ;  $C_{M_2} = C_0 \cdot k_1 / (k_2 - k_1) \cdot (e^{-k_1 t} - e^{-k_2 t})$ ;  $C_{M_3} = C_0 [1 - 1/(k_2 - k_1) \cdot (k_2 e^{-k_1 t} - k_1 e^{-k_2 t})]$ , and it is found that there is a fair agreement between the calculated and observed values. The temperature coefficients for  $k_1$  and  $k_2$  are 1.90 and 1.93 respectively. The addition of electrolytes diminishes the activity of the enzyme, due to the adsorption of them by the enzyme. The effects are calculated by Freundlich's formula for hydrochloric acid,

$h = 1/k_0 \cdot (k_0 - k_1) = 107C^{0.5}$ ; for mercuric chloride,  $h = 108.3C^{0.3}$ ; and for silver sulphate,  $h = 1000C^{0.63}$ . The effect of alkalis is reversible, but that of acids is irreversible. Consequently, the Michaelis relationship,  $\psi'/\psi = 1/(1 + [OH]/g)$ , is applicable to the alkalis, but  $\psi'/\psi = 1/(1 + g/[H'])$  does not hold for acids, because the action of the hydrogen ion is irreversible. J. F. S.

**The Action of Iodine on Arsenious Acid and its Phenyl Derivatives.** PAUL FLEURY (*Bull. Soc. chim.*, 1920, [iv], 27, 490—507).—Iodine reacts with arsenious acid and with the corresponding tervalent phenyl derivatives of arsenic (phenylarsine, diphenylarsine, and triphenylarsine) in the same manner, converting them all into the corresponding arsenic compounds. The action is, however, a balanced one, the hydriodic acid formed tending to reduce the arsenic compounds. In aqueous solution, if their insolubility did not oppose the action, the oxidation of the three phenylarsines would be complete under conditions where arsenious acid would give an equilibrium reaction. Phenylarsine is, however, very sharply distinguished from the di- and tri-phenylarsines, both in the velocity of its oxidation and the equilibrium attained under uniform conditions. The four compounds form a continuous series, in which the oxidisability by iodine increases from arsenious acid up to triphenylarsine. It is of interest to note that both potassium iodide and alcohol, far from diminishing the reducing action of hydriodic acid on the arsenic compounds, rather increase the reduction, and if both iodide and alcohol are present in sufficient concentration, may totally invert the action.

W. G.

**Production of Aromatic Arsenic Compounds [Mono- and Di-aryl Arsenious Haloids].** (Sir) WILLIAM JACKSON POPE (*Brit. Pat.* 142880).—Mono- and di-aryl arsenious haloids are obtained by bringing an arsenious haloid in the liquid or vapour phase into intimate contact with a triarylsarsine heated to a high temperature under ordinary atmospheric pressure. According to the proportion of arsenious haloid employed, reactions expressed by the following equations, in the typical case of the phenyl arsenic chlorides, occur: (1)  $AsPh_3 + 2AsCl_3 = 3AsPh_2Cl$ ; (2)  $2AsPh_3 + AsCl_3 = 3AsPh_2Cl$ ; (3)  $AsPh_3 + AsCl_3 = AsPh_2Cl + AsPhCl_2$ ; (4)  $AsPh_2Cl + AsCl_3 = 2AsPhCl_2$ ; (5)  $AsPhCl_2 + AsPh_3 = 2AsPh_2Cl$ . For these reactions with triphenylarsine a temperature approaching  $350^\circ$  is favourable. The products may be separated by any physical or chemical means, or should the diaryl compound be required as the main product, any monoaryl compound present in the reaction mixture may be converted by gently boiling with triphenylarsine, as expressed by reaction (5) above, and, conversely, should the mono-aryl compound be required, dry diaryl arsenious chloride present is transformed according to reaction (4).

G. F. M.

**Preparation of Aromatic Arsinic Acids.** ANTOINE MOUNEYRAT (Brit. Pat. 142947).—Aromatic arsinic acids are produced by the interaction of aromatic diazonium compounds with cold or warm aqueous or dilute alcoholic solutions of arsenious acid, in acid, neutral, or alkaline medium in the presence of a copper salt and a reducing agent adapted to the acid or alkaline medium employed. In acid medium, for example, hypophosphorous acid or cuprous hydroxide is suitable, whilst in neutral or alkaline medium, sodium hyposulphite, sodium formaldehyde-sulphoxylate, or even an excess of alkaline arsenite may be employed. The method of procedure is capable of numerous modifications in detail, of which examples are given. [See, further, *J. Soc. Chem. Ind.*, 1920, 527A.] G. F. M.

**Arsinic Acids Derived from Guaiacol and Veratrole.** Constitution of the Polyarsenides. ROBERT GEORGE FARGHER (T., 1920, 117, 865—875).

**A Sulphur Compound which is Present in Very Small Amounts in Salvarsan.** C. STRZYZOWSKI (*Korr.-Bl. Schweiz. Aerzte*, 47, 176; *Zentr. Biochem. Biophys.*, 1918, 19, 794. Compare Fargher and Pyman, T., 1920, 117, 372).—The author has detected in salvarsan a sulphur compound, which is possibly a sulpha-acid. CHEMICAL ABSTRACTS.

**Sodium Compound of Diaminodihydroxyarsenobenzene Dihydrochloride.** U. SUZUKI (U.S. Pat. 1330288).—The dihydrochloride is moistened with ethyl alcohol and dissolved in methyl alcohol, and to the solution is added gradually a solution of sodium ethoxide or methoxide until a test portion gives a clear solution in a considerable excess of water. The whole liquid is added to ether containing 6—10% of ethyl alcohol, whereby the desired sodium compound is obtained as a yellowish-brown precipitate, which is washed with ether and dried in a vacuum. The whole process should be carried out in an atmosphere of hydrogen or nitrogen to prevent the possible formation of poisonous or deleterious substances, which may be produced in the presence of even small quantities of oxygen. The product contains 22—23% of arsenic, and its aqueous or physiological sodium chloride solution is suitable for injection. CHEMICAL ABSTRACTS.

## Physiological Chemistry.

**The Analysis of the Carbon Dioxide Equilibrium in Blood According to H. Straub and K. Meyer.** LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1920, 103, 53—59).—A critical discussion of the works of Straub and Meyer (A., 1918, ii, 467;

1919, i, 53; this vol., i, 200) on the combination of hæmoglobin with carbon dioxide. S. S. Z.

**The Catalase of the Erythrocytes.** H. VON EULER and E. BORGSTAM (*Biochem. Zeitsch.*, 1920, 102, 124—131).—The catalase in the erythrocytes of horse's blood is activated by heat. At 57°, an increase in the activity amounting to 170% was observed. Chloroform and toluene activated the catalase only to a small extent. S. S. Z.

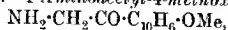
**Serum Lipochrome.** I. A. A. HIJMAN VAN DER BERGH and P. MULLER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 748—757).—Cow's serum was found to contain only carotene, and egg-yolk and fowl's serum only xanthophyll. Human serum usually contained both pigments, with a preponderance of carotene. These are similar observations to those recorded by Palmer (*A.*, 1916, i, 186, 863). The authors do not, however, lend support to the suggestion advanced by the American workers that the lipochrome of cow's serum is present in the form of a complex with protein. Evidence is given that aqueous solutions of carotene, probably colloidal in nature, may be prepared, from which ether will not extract the pigment directly, but only after the addition of alcohol. Other reagents which affect the colloidal state will also "liberate" the carotene, so that it may be extracted by shaking with ether. Carotene in the two forms of solution may show different susceptibilities to destruction by light. J. C. D.

**Hæmolytic Action of some Chlorine Derivatives of Methane, Ethane, and Ethylene.** W. PLÖTZ (*Biochem. Zeitsch.*, 1920, 103, 243—271).—Experiments with a number of chlorine derivatives of methane, ethane, and ethylene show that the hæmolytic activity of these compounds is proportional to their molecular weight and to the number of chlorine atoms. Stalagmometric experiments, on the other hand, have shown that there is no relation between the surface tension of these compounds and their hæmolytic activity. S. S. Z.

**A Thermostat with an Electromagnetic Regulator and Electrical Heating Apparatus.** G. JOACHIMOGLU (*Biochem. Zeitsch.*, 1920, 103, 49—53).—A description of an arrangement of apparatus suitable for experiments with isolated mammalian organs. S. S. Z.

**Sympathomimetic Amines. I. Amino-derivatives of Naphthalene.** A. MADONAVETIA (*Anal. Fis. Quim.*, 1920, 18, 66—78).—The compounds described were prepared to ascertain whether the physiological action of bases related to adrenaline persists in compounds containing a naphthalene instead of a benzene nucleus and an amino-group in the side-chain in the  $\beta$ -position to the nucleus.  *$\beta$ -Methoxy- $\alpha$ -naphthylethylmethyl-*

amine,  $C_{10}H_7\cdot CH(OMe)\cdot CH_2\cdot NHMe$ . The corresponding  $\beta$ -methoxy- $\beta$ -phenylethylmethylamine,  $OMe\cdot CHPh\cdot CH_2\cdot NHMe$ , b. p.  $105-106^\circ$  at 22 mm., was also prepared, as it had not been described previously. 1-Aminoacetyl-4-methoxynaphthalene,



has m. p.  $67^\circ$ .  $\alpha$ -Aminoacetylnaphthalene,  $NH_2\cdot CH_2\cdot CO\cdot C_{10}H_7$ , is described. Tests on the physiological action (constriction of blood vessels) were carried out with the compounds and with  $\beta$ -phenylethylmethylamine used as a standard. The tests proved that a naphthalene compound is forty times more active than a benzene one; that a methoxy-group does not materially affect the physiological properties; and that a carbonyl group in the side-chain decreases, but a hydroxyl group in the nucleus increases, the action of the compound on the blood pressure.

W. R. S.

## Chemistry of Vegetable Physiology and Agriculture.

**Decomposition of *dl*-Phenylalanine by *Bacillus proteus* and *Bacillus subtilis*.** HAJIME AMATSU and MIDORI TSUDJI (*Acta Scholae Med. Univ. Imperial Kioto*, 1918, 2, 441-457).—Each micro-organism (*Bacillus proteus* and *B. subtilis*) was permitted to act in pure culture on a nutrient solution which contained inorganic salts, glycerol, *dl*-phenylalanine, and either a phosphate mixture or lactose plus freshly precipitated uranyl phosphate. Incubation occurred for forty days at  $37^\circ$ . Both bacterial species consumed the *dl*-phenylalanine to a marked degree; that which was recovered after the action of *B. proteus* was dextrorotatory; that which was recovered after the action of *B. subtilis* was optically inactive; apparently *B. proteus* acted asymmetrically, whilst *B. subtilis* attacked both antipodes. Both organisms formed phenyl-lactic acid and phenylethylamine. In the presence of lactose and uranyl phosphate, this amine was formed to a marked degree, but the acid could not be found in the culture. In the presence of a phosphate mixture, the acid was the chief product, and only a very small amount of the amine was formed. *B. proteus* produced *dl*-phenyl-lactic acid, whilst *B. subtilis* made *l*-phenyl-lactic acid.

CHEMICAL ABSTRACTS.

**Formation of Tyrosol from *l*-Tyrosine by Bacteria.** KINSABURO HIRAI (*Acta Scholae Med. Univ. Imperial Kioto*, 1918, 2, 425-432).—A strain of *Bacillus lactis aerogenes*, isolated from the faeces of a breast-fed infant, produced small amounts of tyrosol (*p*-hydroxyphenylethyl alcohol) from *l*-tyrosine during incubation for thirty to thirty-three days at  $25^\circ$  or  $37^\circ$ ; none was formed at  $45^\circ$ . The yield was increased by addition of a phosphate mixture to the nutrient solution, which also contained uranyl phosphate

and either dextrose or lactose. Tyrosol was not obtained by the action of *B. lactis aerogenes* on tyramine hydrochloride. Another strain of this organism did not produce tyrosol from *l*-tyrosine.

CHEMICAL ABSTRACTS.

### The Chemical Composition of the Tubercle bacillus.

A. GORIS (*Compt. rend.*, 1920, 170, 1525—1527).—Tubercle bacilli when washed free from bouillon, dried at 37°, and extracted with chloroform yielded a substance precipitable from chloroform solution by ether, which the author names *hyalitol*, 7 grams being obtained from 1500 grams of dry bacilli. When saponified by sodium hydroxide, the sodium salts of crotonic and isocrotonic acids, and a small amount of a substance having an odour of jasmin and mimosa, are obtained. W. G.

### Action of Different Acids on the Growth of Mucor.

BETTINGER and DELAVAL (*Bull. Assoc. Chim. Suér.*, 1920, 37, 254—261).—The mucor employed for saccharification in distilleries is favourably affected in its vegetative growth by a slight addition of mineral or organic acid to the liquefied cereal mash. The optimum amount of acid varies in a general way inversely with the degree of ionisation, but acetic and succinic acids, which are excretion products, exert a disproportionately great inhibitive action when present in more than the optimum amounts, although their influence is very favourable to growth if this amount is not exceeded. [See also *J. Soc. Chem. Ind.*, 1920, 555A.] J. H. L.

### The Yeast *Saccharomyces thermantitonum*.

HANS VON EULER and INGVAR LAURIN (*Biochem. Zeitsch.*, 1920, 102, 258—268).—A strain of *Saccharomyces thermantitonum* emanating from the Institut für Gärungsgewerbe in Berlin was examined by the authors for its growth, fermentation, and inversion capacities. They found that the limits of temperature characteristic for this species have altered after fifteen years' cultivation in the laboratory on beer wort. A similar observation has been previously made by the authors on a strain of *S. thermantitonum* which came from Jörgensen's laboratory. It is therefore concluded that the yeast, during the years of cultivation in the laboratory, adapted itself to a lower temperature. S. S. Z.

**Formation and Significance of Hexosediphosphoric Acid in the Metabolism of Yeast.** CARL NEUBERG (*Biochem. Zeitsch.*, 1920, 103, 320—336. Compare A., 1918, i. 91).—Fresh bottom yeast in the presence of toluene does not utilise inorganic phosphate, whilst the same yeast after drying esterifies the phosphates. The formation of hexosediphosphate, therefore, does not take place under normal conditions of alcoholic fermentation. S. S. Z.

**Sulphurous Acid and Yeast Fermentation.** ERH HÄGGLUND (*Biochem. Zeitsch.*, 1920, 103, 299—306).—0.007N Sulphurous acid completely inhibited the fermentation of 1 gram

of yeast in 25 c.c. of solution. 0.005*N*-Acid did not completely inhibit its activity. The toxic effect of sulphurous acid on yeast fermentation is attributed to the undissociated acid. Sodium sulphite showed an inhibitive action as compared with potassium sulphate. A 0.2*N*-potassium sulphate solution increased the fermentation by about 25%. S. S. Z.

**Fermentation of Pyruvic Acid under the Conditions of the Fixation Method.** [Fermentation of Pyruvate-Sulphite by Yeast.] CARL NEUBERG and ELSA REINFURTH (*Ber.*, 1920, 53, [B], 1039--1052).—In consequence of the doubts recently cast by Zerner (this vol., i, 350) on the validity of the authors' theory of the intermediate formation of acetaldehyde and pyruvic acid during the course of alcoholic fermentation, the behaviour of the pyruvic acid-sulphite complex has been further studied. It is found that, under greatly varied conditions, the complex is at least as readily fermented by yeast as is pyruvic acid itself. All types of yeast and yeast preparations decompose pyruvic acid in the presence of an equivalent or greater amount of soluble hydrogen sulphites. Under suitable conditions of permeability, which appear to be comparable with the osmotic requirements of sugar fermentation, the pyruvic acid-sulphite complex, in spite of its stability, is more readily fermented than the unstable sugar-sulphite compound. The individual experiments include the fermentation of pyruvic acid in the presence of normal sodium sulphite (1 mol.) by top and bottom yeast, of a molecular mixture of the acid and sulphur dioxide by dry top and bottom yeast, of the pyruvate-sulphite complex by the acetone preparations of either yeast, and by alcohol-ether yeast, of equivalent amounts of pyruvic acid and sodium sulphite by fresh toluidised yeast, and by yeast juice. The fermentation of calcium pyruvate-sulphite and of pyruvic acid in the presence of more than one molecular proportion of sodium sulphite has also been investigated. H. W.

**The Phytochemical Reduction of *o*-Nitrobenzaldehyde.** F. NORD (*Biochem. Zeitsch.*, 1920, 103, 315-320).—Yeast reduces about 10% of *o*-nitrobenzaldehyde to *o*-nitrobenzyl alcohol. The aldehyde group is therefore reduced phytochemically more easily than the nitro-group. S. S. Z.

**The Regulator System: Primary Phosphate-Bicarbonate-Free Carbonic Acid, in place of the System: Primary Phosphate-Secondary Phosphate.** W. WINDISCH and W. DIETRICH (*Biochem. Zeitsch.*, 1920, 102, 141-150).—See this vol., i, 352.

**The Velocity of the Photochemical Decomposition of Carbon Dioxide in Living Cells.** OTTO WARRBURG (*Biochem. Zeitsch.*, 1920, 103, 188-218).—When a cell which has been kept in the dark is exposed to intense light, the velocity of assimilation shows an initial lag before it becomes constant. This lag is



not observed if the cell is exposed to light of low intensity. On submitting the cell to darkness after exposure to intense light, the assimilation gradually ceases. The velocity of assimilation in the cell sinks as the pressure of oxygen increases from one-fiftieth to one atmosphere. The rate of inhibition of the narcotic phenylurethane on the cell is similar to that of the concentration of narcotics as expressed by Freundlich's adsorption curve, which suggests that it is a surface action. Hydrocyanic acid inhibits the photochemical emission of oxygen from carbon dioxide, but not from the intermediate products of respiration formed in the cell; it also inhibits the formation of respiratory carbon dioxide in the cell. Oxygen is split off from nitrates and nitric acid by a suspension of vegetable cells on exposure to light. The kinetics of the photolytic action of the cell in assimilation is discussed.

S. S. Z.

**The Presence of Copper in the Vegetable Organism.** E. FLEURENT and LUCIEN LÉVI (*Bull. Soc. chim.*, 1920, [iv], 27, 440-441).—The authors have extended their work on the presence of copper in plants (compare A., 1911, ii, 445), and have found it to be present in ten other species and to be situated particularly in the leaves.

W. G.

**The Presence of Copper in the Vegetable and Animal Organisms.** E. FLEURENT and LUCIEN LÉVI (*Bull. Soc. chim.*, 1920, [iv], 27, 441-442. Compare preceding abstract).—The percentages of copper found in a number of plants, and also in certain animal products, such as milk, meat, and egg-yolk, are given.

W. G.

**A Case of Favourable Action of Copper on Vegetation.** L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1920, 170, 1542-1545).—Cases are reported where copper sulphate added to water-culture solution exerted a favourable action on the growth of roots and stems of pea and wheat plants during the nine days after germination, and on the root and leaf development of lettuce plants during the thirty-three days after germination. In the first case, 0.2 mg. of anhydrous copper sulphate per litre was used, and for the lettuce 0.02 mg. per litre gave the best results.

W. G.

**Plasmolysing Action of a Certain Number of Vapours.** P. GUÉRIN and CH. LORMAN (*Compt. rend.*, 1920, 170, 1593-1601. Compare Mirande, A., 1910, ii, 884).—The plasmolysis was indicated by the liberation of hydrogen cyanide from the young leaves of cherry laurel or the blackening of the leaves of *Aucuba japonica*. All the alcohols and aldehydes examined exerted a plasmolysing action, as did such substances as *p*-benzoquinone, pyridine, and dichlorobenzene. In certain cases in which Mirande (*loc. cit.*) obtained negative results, the authors have obtained decidedly positive results.

W. G.

**Colloid-chemical Researches on Plant Plasma.** TETSUTARO TADOKORO (*J. Coll. Agr. Hokkaido Imp. Univ., Sapporo, Japan*, 1919, 8, 143—182).—I. *Alteration of the colloidal properties of plasma by the addition of neutral salts.*—The press juice obtained by macerating wheat sprouts 5—8 cm. long with quartz sand was treated with increasing concentrations of various chlorides and with various salts of magnesium. After keeping a certain time, the sedimentation was compared with that of an untreated control. The results show, in general, flocculation by  $\text{AlCl}_3 > \text{BaCl}_2 > \text{SrCl}_2 > \text{CaCl}_2 > \text{MgCl}_2$ , and deflocculation by  $\text{KCl} > \text{NH}_4\text{Cl} > \text{NaCl}$ . Magnesium salts of 0.01N-concentration cause flocculation in the order  $\text{I} > \text{Cl} > \text{NO}_3 > \text{SO}_4 > \text{acetate}$ , but at 0.2N, whilst the iodide shows steadily increasing flocculation, the other cations show deflocculations in the following order:  $\text{SO}_4 > \text{NO}_3 > \text{acetate} > \text{Cl}$ . With 0.1N-calcium salts, flocculation occurs in the following order:  $\text{acetate} > \text{I} > \text{NO}_3 > \text{Cl}$ . Comparing these results with those of other investigators, it is found that salt concentrations which poison wheat also cause colloidal changes in the press juice. II. *Antagonism and the alteration of the plasma colloids.*—Experiments showing the antagonism between various salts in their action on press juice of wheat sprouts were paralleled by pot-culture experiments showing a corresponding effect of the same mixture on the growth of the wheat plant. The following pairs of salts were used:  $\text{NaCl}-\text{CaCl}_2$ ,  $\text{KCl}-\text{CaCl}_2$ ,  $\text{KCl}-\text{MgSO}_4$ ,  $\text{K}_2\text{SO}_4-\text{MgCl}_2$ ,  $\text{CaCl}_2-\text{MgCl}_2$ ,  $\text{CaCl}_2-\text{MgSO}_4$ . The essential basis of antagonism lies in the maintenance of a certain optimum degree of colloidal dispersion, which the author terms "life-colloidal." For example, sodium chloride tends to deflocculate and calcium chloride tends to flocculate, so that the proper balance between them maintains the optimum dispersion. In like manner, asparagine, glycine, and peptone produce flocculation of press juice in increasing order, whilst sucrose, dextrin, and dextrose produce deflocculation. Therefore, as experiments demonstrate, dextrose is antagonistic to calcium chloride, whereas glycine is antagonistic to potassium chloride. Two other series of experiments show that the same basis of antagonism extends to diffusion through the press juice of *Brassica* leaves, and to the effect of the salts, etc., on the enzymic action of wheat sprout amylase and taka-diastase.

CHEMICAL ABSTRACTS.

**A Quantitative Study of the Effect of Anions on the Permeability of Plant Cells.** ORAN L. RABER (*J. gen. Physiol.*, 1920, 2, 535—539).—The salts used were all sodium salts, the solutions having  $p_H = 7 \pm 0.5$ , and their effects on the permeability of *Laminaria agardhii*, Kjellm., were determined. When these salts were used in solutions having the same conductivity, the anions arranged themselves in the order  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{CNS}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{CH}_3\text{CO}_2^-$ ,  $\text{SO}_4^{--}$ ,  $\text{C}_2\text{H}_4\text{O}_2(\text{CO}_2)_2^{--}$ ,  $\text{PO}_4^{--}$ ,  $\text{C}_2\text{H}_3\text{O}_2(\text{CO}_2)_3^{--}$  as regards their effect on the permeability, there being thus slight differences from Hofmeister's series. Where the salts were used in equimolecular solutions, the series became  $\text{CNS}^-$ ,  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ .

$\text{CH}_3\text{CO}_2^I$ ,  $\text{SO}_4^{II}$ ,  $\text{C}_2\text{H}_3\text{O}_2(\text{CO}_2)_2^{II}$ ,  $\text{PO}_4^{III}$ ,  $\text{C}_3\text{H}_5\text{O}(\text{CO}_2)_2^{II}$ , the salts apparently forming themselves into two distinct groups. W. G.

**The Antagonistic Action of Anions.** ORAN L. RABER (*J. gen. Physiol.*, 1920, 2, 541—544).—Distinct antagonism is shown between the acetate and sulphate anions when used as their sodium salts in their effect on the permeability of *Laminaria*. W. G.

**Presence in Melilotus and Asperula odorata of Glucosides yielding Coumarin under the Hydrolysing Action of Emulsin.** EM. BOURQUELOT and H. HÉRISSEY (*Compt. rend.*, 1920, 170, 1545—1550).—Three species of *Melilotus* and *Asperula odorata* were all found to contain a glucoside, which, under the influence of emulsin, gave coumarin. It is probable that the glucoside which yields coumarin varies from one plant species to another. W. G.

**The Alkaloid Constituents of Rice Polishings.** FRANZ HOFMEISTER [with MASAHITO TANAKA] (*Biochem. Zeitsch.*, 1920, 103, 218—225).—The author has isolated from rice an alkaloid substance, *oridine*, which possessed anti-neuritic activity, but on purification, it became inactive. The hydrochloride was prepared as follows: Rice meal was extracted with 80% alcohol. The alcoholic extract was evaporated to a syrup in a vacuum, and made up with hydrochloric acid to a solution containing 3% of the acid. After extraction of impurities with ether, the acid solution was concentrated again to a syrup and made feebly alkaline with sodium carbonate, and precipitated with bismuth-potassium iodide solution. After acidifying the filtrate, the precipitation was repeated, and the precipitate was triturated with silver carbonate and decomposed with hydrochloric acid. The substance was then obtained in crystalline form on drying the filtrate. Doses of 5–10 mg. of the hydrochloride were found to be active. The *aureichloride*,  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2\text{HAnCl}_2$ , formed platelets and flat prisms, m. p. 277°. *Oridine hydrochloride*,  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2\text{HCl}$ , forms colourless prisms, m. p. 240°. The free base was a white, hygroscopic powder, soluble in water. It was found to be isomeric with betaine and valine, and, according to its properties, it is conjectured to be related to the pyridine and piperidine groups. S. S. Z.

**The Mosaic Disease of Spinach as Characterised by its Nitrogen Constituents.** S. L. JODID, S. C. MOULTON, and K. S. MARKLEY (*J. Amer. Chem. Soc.*, 1920, 42, 1061—1070).—Previous work on the nitrogen metabolism of the spinach plant (*J. Agric. Research*, 1918, 15, 372, 381, 385) had led to the assumption that denitrification takes place in the diseased plant. With the object of corroborating this, material from other fields and another year has been examined. It is thus shown that the mosaic disease is accompanied by a lower total, and also nitric, nitrogen content,

but a higher ammoniacal nitrogen content of the diseased leaf tissue. Further, nitrites are present in diseased but not in healthy leaves. Probably as a result of this, the basic (diamino-) and non-basic (monoamino-) nitrogen content of diseased leaf tissue is less than that of healthy tissue. The proportion of protein nitrogen and protein in healthy leaves is greater than in the roots, but in diseased material there is practically no difference, the actual percentages being greater in the latter case, with the exception that the leaves show a higher protein content in health than in disease. It is therefore concluded that denitrification of leaves, but not of roots, is characteristic of mosaic disease. J. K.

**The Unsaturated Alcohol of the Essential Oil of Freshly Fermented Tea Leaves.** P. VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 758-761).—The alcohol is  $\gamma$ -hexene- $\alpha$ -ol, identical with that obtained by Walbaum from Japanese oil of peppermint (A., 1918, i, 302). J. C. D.

**Action of Gaseous Chlorine and Bromine on Medicinal Plants.** DOMENICO LAOTTA (*Arch. Farm. sper. Sci. off.*, 1919, **28**, 152-160, 161-169).—When treated with chlorine or bromine, the leaves of *Nerium oleander* and of *Digitalis purpurea* completely lose their toxic properties. Experiments made with the leaves of *Prunus laurocerasus* yielded no definite results, but the leaves employed were gathered in November, at which time they are almost devoid of amygdalin.

Similar tests were made with leaves of *Pilocarpus pinnatifolius*, *Arnica montana*, *Nicotiana tabacum*, *Atropa belladonna*, *Lobelia inflata*, and *Aconitum napellus*. In these cases, the aqueous extracts of the leaves are turbid and difficult to filter, but become limpid and easy to filter after the leaves have been treated with chlorine or bromine. In those cases where the aqueous extract causes death, the aqueous extract of the treated leaves produces the same effect.

With the former group, the halogen apparently produces hydrolysis of the glucoside present, whereas, with the latter, a salt of the alkaloid is probably formed. The action of chlorine or bromine may serve to decide whether the active principle of leaves is glucosidic or alkaloidal in character, and such treatment furnishes a simple means of extracting alkaloids from vegetable or animal substances. T. H. P.

**Acidity and Acidimetry of Soils. II. Investigation of Acid Soils by means of the Hydrogen Electrode.** HENRY G. KNIGHT (*J. Ind. Eng. Chem.*, 1920, **12**, 457-464. Compare this vol. i, 468).—A hydrogen electrode cell suitable for use in soil investigations is described, as are also the results of experiments on the rate of reactions between normal salt solutions and soils, the rate of reaction in the presence of a base, the change in hydrogen ion concentration with change of amount of base and

with time, and the change in conductivity of soil solutions. [See, further, *J. Soc. Chem. Ind.*, 1920, 523A.] W. P. S.

**Relative Absorption by Soil of Sodium Carbonate and Sodium Chloride.** THOMAS H. KEARNEY (*Soil Sci.*, 1920, 9, 267—273).—Observations on plants growing in alkali soils have shown that sodium carbonate is more toxic than sodium chloride, whereas many laboratory experiments on the toxicity of added salts have given the reverse result. Experiments were made to determine whether this difference was due to differences in the amount of absorption of the salts by the soil producing soil solutions of very different concentrations. Solutions of sodium carbonate and sodium chloride of varying concentration were added to sand, and after leaving for twenty-four hours for absorption to become complete, the electrical resistance of the sand was determined by the bridge method. The results obtained showed that 63% of the sodium carbonate was absorbed from solution by the sand, whereas only 23% of the sodium chloride was absorbed.

J. H. J.

**The Absorbent Power of Soil with Respect to Manganese** P. NOTTIN (*Compt. rend.*, 1920, 171, 44—47).—Compost or tur absorbs manganese from solutions of manganous salts to a far greater extent than does ordinary soil. This the author attributes to a difference in the crystallographic state of the calcium carbonate present in the soil. He shows that calcite is not acted on by a 1% solution of manganous chloride, whilst aragonite or kryptite is dissolved to a very large extent, and an appreciable amount of manganese is thrown out of solution.

W. G.

**Effect of Calcium Sulphate on the Solubility of Soils** M. M. MCCOOL and C. E. MILLAR (*J. Agric. Res.*, 1920, 19, 47—54).—Six soils of different types were treated with a saturated solution of calcium sulphate for twenty-four hours. In one series the soil was then simply drained on a filter, and in another series it was washed with distilled water until the amount of soluble material was reduced to a minimum. In both series, the rate of formation of soluble substances at high and low water content was then determined by the freezing-point method and compared with that for untreated soil. In every case, the treatment was found to have caused a very large increase in the rate of formation of soluble substances. Similar treatment with a  $N/10$  solution of calcium phosphate, on the other hand, decreased the rate of formation of soluble substances, and when used with calcium sulphate, decreased its effect.

If the carbon dioxide produced may be taken as a measure of biological activities, the effects described above cannot be ascribed to increase in biological activity, but require some other explanation.

W. G.

## General and Physical Chemistry.

**Secondary Spectrum of Hydrogen.** MEGH NAD SAHA (*Phil. Mag.*, 1920, [vi], **40**, 159-161).—A reconsideration of the calculations of Fabry and Buisson (*A.*, 1912, ii, 613) leads to the conclusion that if the H $\alpha$  line is emitted by a hydrogen atom, the secondary lines are emitted by the hydrogen molecule. J. R. P.

**Structure of the Balmer Series of Hydrogen Lines.** T. R. MERTON (*Proc. Roy. Soc.*, 1920, [A], **97**, 307-320).—The H $\alpha$  and H $\beta$  lines have been examined by means of an échelon diffraction grating of thirty-five plates, 15.085 mm. thick, and with a grating step of 0.83 mm. The light was subjected to a preliminary analysis by means of a constant deviation spectroscope before passing into the échelon. It is shown that in tubes containing hydrogen and helium at a few millimetres pressure, the resolution of H $\alpha$  is complete, whilst H $\beta$  shows no definite structure. On cooling the spectrum tube with liquid air, the H $\alpha$  line appears as a sharp doublet, perfectly resolved, and H $\beta$  also appears as a definite doublet, but the components are not completely resolved and are hazy in appearance. In the case of the H $\alpha$  doublet, the separation of the components is 0.1446 Å, and the intensities of the components are in the ratio 10:4.6, whilst for H $\beta$  the separation is 0.093 Å. The half-width of the components is H $\alpha$ , 0.023 Å; H $\beta$ , 0.045 Å. The author is of the opinion that the observations cannot be explained on the basis of simple doublets, and that it is probable that these lines consist of three or more components, which show great variability in their relative intensities under different conditions. J. F. S.

**Spectra and Atomic Numbers of the Elements.** J. E. JACULSON (*Astrophys. J.*, 1919, **49**, 276-281).—Rydberg's relation between the frequency-difference of certain spectral lines and the atomic weight,  $10^8 \nu / P^2$ , where  $\nu$  is the frequency-difference and  $P$  the atomic weight, is based on a unit which is not fundamental, and the substitution of atomic number for atomic weight gives a better relation. Taking Rydberg's atomic numbers ( $E=0$ ,  $H=1$ ,  $I=2$ ,  $Fe=3$ ,  $He=4$ ,  $Li=5$ , etc.), frequency-differences are calculated on the basis of the two formulae,  $\nu = A \log (N + n) + B$  and  $\nu = A \log (P + n) + B$ , where  $N$  is the atomic number,  $A$  and  $B$  are constants computed by the method of least squares, and  $n$  is a whole number, generally small, which may be positive or negative. For the groups of metals examined, the formula for atomic numbers agrees much better with observed frequencies.

CHEMICAL ABSTRACTS.

**Atomic Theory and Low Voltage Arcs in Cæsium Vapour.**

PAUL D. FOOTE and W. F. MEGGERS (*Phil. Mag.*, 1920, [vi], **40**, 80—97; *J. Opt. Soc. Amer.*, 1920, **4**, 145—147).—The normal operation of an arc below ionisation may result in the excitation of a single-line spectrum, a single-series spectrum, or a group spectrum consisting of lines of different series. An explanation is offered of fluorescence in vapours of alkali metals. A mechanism of absorption of radiation is described. The cæsium spectrum was photographed for various accelerating voltages from  $\lambda$  3878 to  $\lambda$  9208 with plates stained with dicyanin. No evidence of group or single-series spectra was found. The doublet,  $1\cdot5s-2p_1$  is alone produced under excitation of 1·5 to 3·9 volts accelerating field. The intensity of these lines gradually increases approximately in proportion to the total number of electrons reaching the anode until the ionisation potential is reached. At this point, a pronounced decrease in intensity occurs, this decrease taking place at the voltage at which the complete line spectrum is produced. This affords a strong argument for Bohr's theory. After a certain voltage, the intensity of any line per unit number of electrons reaching the anode attains a saturation value, in agreement with the quantum hypothesis. Only two types of inelastic impact between electrons and atoms of the alkali metal vapours occur, at the resonance and ionisation potentials respectively, and given by the quantum relation  $h\nu = eV$ , where  $\nu = 1\cdot5s-2p_1$  and  $\nu = 1\cdot5s$ .

J. R. P.

**Extreme Ultra-violet Spectra of Magnesium and Selenium.**

J. C. McLENNAN, J. F. T. YOUNG, and H. J. C. IRETON (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 67—72).—The spectrum of magnesium for spark in air and arc in air has been investigated in the region between 2026 and 1850 Å.U., and seven new lines recorded. The spectrum of the magnesium arc in a vacuum has been investigated in the region between 2300 and 1400 Å.U., and seven new lines measured. Several of these agree with lines found by Saunders with the spark in hydrogen, and by Handke with the spark in air. The series  $\nu = (1\cdot5s) - (m, p)$  has been verified for values of  $m$  from 2 to 6, but experiments have failed to detect any further lines of the series  $\nu = (1\cdot5s) - (m, p_2)$ , beyond, possibly, the second member. Thirty lines have been recorded in the selenium arc spectrum between 2300 and 1400 Å.U.

J. R. P.

**Metallic Spectra Produced in High Vacua.**

EDNA CARTER and ARTHUR S. KING (*Astrophys. J.*, 1919, **49**, 224—236).—Spectra of manganese, titanium, iron, magnesium, calcium, and cadmium were produced by vaporising the metals at the focus of a beam of cathode rays and photographing the luminescence in the path of the rays. The metallic vapour in all cases except iron assisted the evacuation by absorbing gas molecules, but iron did not, and in order to vaporise it, it was necessary to make the anticathode

the anode. The lines excited were generally those of the arc and furnace spectra, with the following peculiarities: Certain arc and furnace lines are intensified, whilst others are weakened or absent. The tendency to give enhanced lines, that is, the resemblance to the arc spectrum, is marked in the case of cadmium, present also in the cases of magnesium and calcium, but is very slight for iron, manganese, and titanium. Single-line series show a relatively greater intensity than other series lines. The intensity of the ultra-violet lines is relatively high as compared with the arc and furnace spectra.

CHEMICAL ABSTRACTS.

**Arc Spectrum of Cobalt According to International Normals.** FERDINAND DIEHL (*Zeitsch. Wiss. Photochem.*, 1920, 19, 289—335).—The arc spectrum of cobalt has been measured by means of a concave grating 6.54 metres radius and 20,000 lines per inch. Granular cobalt was placed in a carbon arc burning with a current of 4—6 amps. at 150 volts, and served as the source of light in all measurements. An iron arc was used for the comparison spectrum. The wave-lengths and intensities of 1,384 lines between  $\lambda$  7417.38 and  $\lambda$  2590.606 are recorded in tables and compared with measurements of Krebs (*Diss. Bonn*, 1916). The lines due to impurities, nickel, iron, manganese, calcium, copper, silver, titanium, aluminium, magnesium, and vanadium are recorded in other tables.

J. F. S.

**Absorption Spectra of Thallium, Aluminium, Lead and Tin, and Arsenic.** J. C. McLENNAN, J. F. T. YOUNG, and H. J. C. IRETON (*Trans. Roy. Soc. Canada*, 1919, 13, iii, 7—13).—In addition to the absorptions of thallium discovered by Guthrie (*Diss. Baltimore*, 1908), further absorptions were obtained as arc reversals. These additional absorptions in the ultra-violet region were confined to the two series,  $v=(2.p_2)-(m,d')$  for values of  $m=6$  to 14 inclusive, and  $v=(2.p_2)-(m,s)$  for  $m=5.5$  to 11.5 inclusive. The series  $v=(2.p_2)-(m,s)$  has been observed for values of  $m=10.5$  and  $m=11.5$  for the first time. No absorption was obtained in the region 1700 Å.U. with the thallium arc in a vacuum. The absorption spectrum of aluminium consists of fourteen bands in the extreme ultra-violet. As with thallium, these absorptions are given by the series,  $v=(2.p_2)-(m,d')$  for values of  $m=6$  to 14 inclusive, and  $v=(2.p_2)-(m,s)$  for values of  $m=4.5$  to 8.5 inclusive. The series  $v=(2.p_2)-(m,d')$  has been verified for  $m=12$ , 13, and 14, and the series  $v=(2.p_2)-(m,s)$  for  $m=6.5$  and 7.5, for the first time. In all, nineteen absorption bands of lead were measured. It is possible that the system of narrow and diffuse absorptions may correspond with the analogous series absorptions of thallium and aluminium. Three absorption bands of tin were obtained, but no identification of series is yet possible. The flame spectrum of arsenic consists of five lines: 3266, 2860, 2780, 2350, and 2288 Å.U., together with four bands with heads at 2634.5, 2570, 2503.5, and 2437.3 Å.U. The arc absorption spectrum con-



sists of four strong unilateral bands, the sharp edges of which were towards the red, and occurred at wave-lengths 2634.5, 2670.0, 2503.5, and 2437.31 Å.U. Contrary to expectation, no single-line absorption or emission was found which could possibly be supposed to correspond with the line 2620 Å.U. predicted by Foote and others. J. R. P.

**The Absorption Spectra of the Cobalt Dithiocarbamates and Xanthates.** MARCEL DELÉPINE and LOUIS COMPIN (*Bull. Soc. chim.*, 1920, [iv], 27, 474—477).—A comparative study of the absorption spectra of certain of the cobalt xanthates and dithiocarbamates previously described (this vol., i, 522, 536) shows that, from the point of view of absorption, the group  $\text{CS}\cdot\text{S}_3\text{Co}$  dominates all the singularities of the rest of the molecule. W. G.

**Absorption of Light by Methæmoglobin in Neutral Solution and in Solution made Alkaline by Sodium Carbonate.** PAUL HÄRI (*Biochem. Zeitsch.*, 1920, 103, 271—292).—There is a marked difference in the spectroscopic behaviour of methæmoglobin in neutral solution and in solution made alkaline by sodium carbonate. It is suggested that in alkaline solution, methæmoglobin is reconverted into oxyhæmoglobin, and is probably also changed into other hæmoglobin derivatives. S. S. Z.

**Light Absorption and Fluorescence. VI. Atomic and Molecular Energy Quanta. VII. Molecular Phases.** E. C. C. BALY (*Phil. Mag.*, 1920, [vi], 40, 1—14, 15—31. See A., 1915, ii, 605; 1916, ii, 240).—VI. From the conception of the elementary energy quantum required to shift one electron from one stationary orbit to another, and the simple assumption that the combining atoms share equally in the energy loss on combination and in the future energy changes of the resulting molecule, the author arrives at the conception of molecular quanta and molecular frequency, the latter being the least common multiple of the atomic frequencies. The smallest possible equal amounts of energy which two or more atoms can evolve when combining together are equal to one quantum measured at the frequency which is the least common multiple of their atomic frequencies. The molecule may also exhibit those frequencies which are characteristic of its component atoms. These conceptions are applied to the elucidation of the observed relationships between the absorption frequencies of compounds.

VII. Chemical reactivity of atoms is due to the attraction exerted by their electromagnetic fields. As a result of this attraction, an additive complex is formed as a first stage in the reaction. The second stage is the joint loss by all the atoms of equal amounts of energy, and the formation of a freshly synthesised molecule with its infra-red fundamental. The reactivity of molecules is a function of their force fields, and the first stage of any reaction between two or more molecules is the formation of an additive

complex, due to the attraction of their force fields. The reactivity of a molecule will depend on the molecular phase in which it exists; the greater the condensation which has occurred in the force field, the less will be the reactivity.

J. R. P.

**The Photochemical Equivalent Law from the Point of View of the Bohr-Einstein Conception of Light Absorption.** O. STERN and M. VOLMER (*Zeitsch. wiss. Photochem.*, 1920, 19, 275—287).—A theoretical paper in which the discrepancy between the Einstein equivalent law  $n = E/h\nu$  is explained by means of Bohr's conception of light absorption.

J. F. S.

**Mathematical Theory of Photochemical Kinetics.** J. PROTNIKOV (*Zeitsch. wiss. Photochem.*, 1920, 19, 225—274, 335—348).—A mathematical paper in which, after a general introduction to photochemical kinetics, the author develops the kinetic relationships of irreversible photochemical reactions for the normal case where there is a moderate absorption of light, and also for the limiting cases where there is, respectively, a very strong and a very weak absorption of light. The special cases of polychromatic light, mirror action, and also reactions with circulating reagents and those occurring in cylindrical vessels, are considered, and mathematical relationships developed for them. Reactions which occur in laminæ are dealt with, and the conditions are established for filter action, both internal and external. The author also considers photo-reactions which are accompanied by non-photochemical reactions, and reactions of one photo-active component for the conditions (a) where there are two separated photo-active absorption bands, and (b) where there are two partly superposed photo-active absorption bands. The case of two active components is considered (a) where one component is photo-active and the other is not, and (b) where both components are photo-active. The influence of temperature and the order of photochemical reactions are treated, and, finally, the special case is discussed where an inactive component constitutes a light filter.

J. F. S.

**The Action of Phosphorus, during Oxidation, on the Photographic Plate and its Ionising Power.** W. P. JORISSEN (*Rec. trav. chim.*, 1920, 39, 429—434).—A reply to Centnerszwer and Petrikaln (compare A., 1912, ii, 709).

W. G.

**The Cleavage of Lactic Acid by Rays of Short Wave-lengths.** OSKAR BAUDISCH (*Biochem. Zeitsch.*, 1920, 103, 59—63).—The author could not confirm Euler's observation that, on exposing lactic acid to the light of a quartz mercury vapour lamp, alcohol is formed (A., 1911, ii, 452; 1912, ii, 497), nor could he confirm the formation of methane by this exposure, as was alleged by Schanz (*Arch. ges. Physiol.*, 1918, 71, 650). Acetone, according to the author, does not form methane and acetic acid by being exposed in dilute aqueous solution to sunlight for a short time. These products are formed after an exposure of several months.

S. S. Z.

**Action of Radiations of Different Wave-lengths on Chlorophyll.** RENÉ WURMSER (*Compt. rend.*, 1920, 170, 1610—1612).—In the action of light on chlorophyll in acetone solution in the red, green, and violet portions of the spectrum, it is shown that the photochemical susceptibility varies with the wave-length in a manner proportional to the constant of absorption, except in the neighbourhood of the minimum of absorption, where it decreases more rapidly. The radiations, the frequencies of which correspond with the two principal bands, red and violet, of the chlorophyll, are, for equal absorbed energy, equally active.

W. G.

**The Absorption of X-rays.** R. A. HOUSTON (*Proc. Roy. Soc. Edin.*, 1920, 40, 34—42).—An expression used to denote the variation of the coefficient of absorption through an absorption band in optics is applied to the absorption bands of the *J*-, *K*-, and *L*-homogeneous X-radiation, and it is shown that from it can be deduced the number of electrons per atom taking part in the production of the radiation. The seven results given for *K*-rays do not differ greatly from unity, which is the same result as was deduced similarly by the author for the absorption bands of aniline colouring matters and inorganic salts (*Proc. Roy. Soc.*, 1909, [A], 82, 606). The mean value by one method of calculation is 0.972, and by another 1.01. For the *L*-bands of platinum and gold, the bands appear to be double with either one or two electrons concerned per component, that is, 2 or 4 in all. But for the *J*-bands the result (0.002 for aluminium) suggests that a singly charged hydrogen atom or doubly charged helium atom rather than an electron is the operative cause. The results furnish an independent confirmation of the wave-length of the X-rays, and tell against Bohr's model.

F. S.

**The Law of Mass-Absorption of the Röntgen Rays.** F. BUTAVAND (*Ann. Physique*, 1920, [ix], 13, 161—168).—An empirical and approximate relation is shown to hold between the mass-absorption coefficient  $\lambda/\rho$ , where  $\lambda$  is the absorption coefficient and  $\rho$  the density, and the atomic weights  $P_e$  of the emitting element and  $P_a$  of the absorbing element, which, deduced step by step for each series of rays, takes the general form

$$(\lambda/\rho)_a^{(n)} P_e/P_a^{(n)} = 13.4 \cdot 2^{n-1};$$

$n$  refers to the type of radiation, and has for the four series *H*, *J*, *K*, *L* the values 1, 2, 3, 4 respectively.

In the table, the first column refers to the type of radiation, the second to the value of  $n$ , the third to the experimental value of the above expression on the left-hand side of the above equation, and the fourth to that calculated from the right-hand expression.

<i>H</i> .....	$n=1$	14	14
<i>J</i> .....	2	17	17.5
<i>K</i> .....	3	29	26
<i>L</i> .....	4	77	77

A graphical representation of these results leads to the suggestion that there exist two series to be discovered, designated *G* and *M*, the first very "hard" with the value in the last column corresponding with 13.25, and the second very "soft" with the value 270.

F. S.

**The Measurement of Radium Emanation in Spring Waters.** H. GREINACHER (*Physikal. Zeitsch.*, 1920, **21**, 270—272).—A method is described of carrying out the measurements of radium emanation in spring waters by means of small vessels, of 2 litres capacity or less, in place of the large 10- or 15-litre vessels usually employed. The volume of water,  $V_0$ , put into a can of volume  $V$  is arranged to be equal to  $V/(1 + \sqrt{a})$ , where  $a$  is the absorption coefficient of the emanation in water. After shaking, the water is run out and fresh air admitted to take its place. The emanation in the vessel is then measured. Particulars are given for the reduction of the results to Macho units.

F. S.

**New Determination of the Absolute Value of the Radium: Uranium Ratio.** S. C. LIND and L. D. ROBERTS (*J. Amer. Chem. Soc.*, 1920, **42**, 1170—1177).—A standard radium solution was prepared by dissolving 0.2067 gram of 100% radium chloride containing 157.3 mg. of radium in 1 litre of 5% redistilled hydrochloric acid. The radium content of the specimen was controlled by the  $\gamma$ -ray method by comparison with the International radium standard. The clear solution was diluted with 5% hydrochloric acid until 1 litre contained  $1.573 \times 10^{-6}$  gram of radium, protected by one million times as much barium chloride. This standard solution was used to standardise three electroscope chambers, each of which had two interchangeable leaf chambers. The standardisation was effected by the Bureau of Mines method (emanation method). The same electroscopes were also standardised by the U.S. Bureau of Mines pitchblende standard. The results give as a final average of eighteen determinations,  $3.40 \times 10^{-7} \pm 0.03$  for the ratio radium:uranium. The result agrees with the results of Becker and Jannasch,  $3.399 \times 10^{-7}$  (*Jahrb. Radioaktiv. Elektronik*, 1915, **12**, 1—31), and Rutherford and Boltwood,  $3.4 \times 10^{-7}$  (*A.*, 1905, ii, 568; 1906, ii, 593; 1908, ii, 451; 1911, ii, 788).

J. F. S.

**The Determination of the Radioactivity of Spring Waters.** OTTOMAR NÜRNBERGER (*Physikal. Zeitsch.*, 1920, **21**, 241—245).—Investigations were made on the radioactivity of a group of springs near Brambach, Saxony, by a variety of the special apparatus designed for this work. It was found that the rate of increase of the activity with time for the emanation was different for each spring and characteristic of it, and departed from that obtained for a solution of pure emanation. These differences are attributed to salts and gases dissolved in the natural spring water.

F. S.

**The Separation of Isotopes.** ALEXANDER FLECK (*Nature*, 1920, 104, 565).—It is suggested, as a method of testing further the chemical separability of isotopes, that an ester, such as ethyl acetate, should be saponified with baryta containing radium and its isotope, mesothorium-1, and the ratio of the two isotopes estimated in the salt formed during the progress of the reaction. If the ratio is unchanged through the reaction, it will indicate that their reactive powers or strengths as bases are the same. F. S.

**Nomenclature Questions concerning Isotopes.** F. SEKERA (*Jahrb. Radioaktiv. Elektronik.*, 1920, 16, 411–415).—A discussion of such terms as Misch elemente, element typus, and Bleiart in use in Germany in connexion with isotopes. F. S.

**Ionisation and Resonance Potentials of Nitrogen, Oxygen, and Hydrogen.** F. L. MOHLER and PAUL D. FOOTE (*J. Opt. Soc. Amer.*, 1920, 4, 49–54).—The ionisation and resonance potentials have been measured for hydrogen, oxygen, and nitrogen by the methods previously used for the measurement of the critical potential of electron currents in metallic and non-metallic vapours (*A.*, 1918, ii, 94, 287; 1919, ii, 42). In the case of nitrogen, by three methods, the resonance potential is found to be  $8.18 \pm 0.10$  volts, and the ionisation potential  $16.9 \pm 0.5$  volts. The resonance potential corresponds with the nitrogen doublet at  $\lambda = 1492.8 \text{ \AA}$  and  $\lambda = 1491.8 \text{ \AA}$ , whilst the ionisation potential corresponds with the first term of the series converging at  $\lambda = 730 \text{ \AA}$ . The resonance potential,  $7.91 \pm 0.1$  volts, was obtained for oxygen, and the ionisation potential has the value  $15.5 \pm 0.5$  volts. These values indicate that  $\lambda = 1570 \text{ \AA}$  is the single-line spectrum of oxygen and the first member of a series converging at  $\lambda = 800 \text{ \AA}$ . Hydrogen has a resonance potential at 10.4 volts, the first ionisation potential is 13.3 volts, and the second 16.5 volts. The first ionisation potential is for the atom and the second for the molecule, the difference should give the heat of dissociation per gram-molecule of hydrogen. This value is 74,000 cal., whereas Langmuir calculates the value 90,000 cal., and the value derived from Bohr's theory is 65,000 cal. The first ionisation potential is difficult to measure, and if the value be taken as 13.5, the value 65,000 cal. would then follow. There is evidence of a slight resonance collision between 2.5 and 3.5 volts, but the value has not yet been accurately fixed. J. F. S.

**Extrapolation of Conductivity Data to Zero Concentration.** II. EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1920, 42, 1077–1087. Compare *A.*, 1918, ii, 55).—The author's method of obtaining the value of  $\Lambda_\infty$  has been criticised by Kendall (*A.*, 1918, ii, 182) and Kraus (this vol., ii, 217). In the present paper, the author discusses the points which have been criticised. In answer to Kendall's claim for priority, it is shown that the method used by Kendall is only possible when the electrolyte obeys the law of mass action, whilst the method under

discussion is possible, irrespective of whether the electrolyte obeys the law of mass action or not. In answer to Kraus, it is shown that the assumptions in the two cases are diametrically opposed. Mathematically expressed, Washburn writes

$$\lim_{c \rightarrow 0} 1/K_E \cdot dK_E/dC = 0,$$

whilst Kraus writes  $\lim_{c \rightarrow 0} 1/K_E \cdot dK_E/dC = -\infty$ .

J. F. S.

#### Extrapolation of Conductivity Data to Zero Concentration.

CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1920, **42**, 1087—1090. (Compare preceding abstract).)—An answer to Washburn's paper (*loc. cit.*), in which it is shown that Washburn's results are a necessary consequence of the assumptions made. It is further shown that, whilst Washburn's method may be applicable to any form of curve and at any concentration, the value of  $\Lambda_0$  will be different for the different concentrations and for the different forms of curve, save in the exceptional case that  $\Lambda$  is a linear function of the concentration, in which case the law of mass action is actually obeyed.

J. F. S.

#### Extrapolation of Conductivity Data to Zero Concentration.

EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1920, **42**, 1090—1091. Compare preceding abstracts).—An answer to Kraus, in which the author states that Kraus's criticism indicates that his method of extrapolation has been misunderstood. He therefore applies it to measurements of Wieland, and draws curves to show that, without using any assumption or smoothed curve, the value of  $\Lambda_0$  for potassium chloride lies at 129.65.

J. F. S.

#### Theory of Electrolytic Ions. XVI. Electrical Conductivity of the Arsinic Acids.

RICHARD LORENZ and ERIKA SCHMIDT (*Zeitsch. anorg. Chem.*, 1920, **111**, 175—192. Compare this vol., ii, 482).—The electrical conductivity of arsanilic, *o*-aminotolylarsinic, diaminophenylarsinic, *m*-dihydroxyphenylarsinic, 3-nitro-4-aminophenylarsinic, dichlorophenylarsinic, 3-nitro-4-hydroxyphenylarsinic, *m*-nitrophenylarsinic, and phenylene-1:4-diarsinic acids have been determined at dilutions 1/64—1/1028, and the conductivity at infinite dilution has been extrapolated in each case. The conductivities of the following acids at infinite dilution have been obtained: arsanilic, 370.0; *o*-aminotolylarsinic, 369.0; diaminophenylarsinic, 369.0; *m*-dihydroxyphenylarsinic, 371.0; 3-nitro-4-aminophenylarsinic, 369; dichlorophenylarsinic, 371.0; 3-nitro-4-hydroxyphenylarsinic, 370.0; phenylene-1:4-diarsinic, 369.0; *m*-dinitrophenylarsinic, 369.0.

J. F. S.

#### Measurement of Dielectric Constants using High Frequencies with a Wheatstone's Bridge.

HANS JOACHIM (*Ann. Physik*, 1919, [iv], **60**, 570—596).—The measurement of dielectric constants by means of a modified Hertwig apparatus is described (*ibid.*, 1913, **42**, 1099). It is shown that by the introduction of an ionic tube generator, it is possible to carry out the measurements with undamped waves of constant amplitude. The

apparatus is silent and very simple. In the same way, it is possible to use the Nernst method for measurements with rapid oscillations. A number of measurements with various substances are given as a test of the suitability of the method. The dielectric constant of potassium chloride (2.06), potassium alum (2.970), lead chloride (4.29), lead sulphate (3.72), lead formate (2.35), amorphous sulphur (2.84), mercuric chloride (2.58), mercuric cyanide (2.41), and ammonium sulphate (2.56) in the powdered condition has been determined; the values in these cases are indicated in brackets. The temperature-coefficient has been determined down to  $-180^{\circ}$  for several of the substances. The theory of the dependence of the dielectric constant on temperature, the rôle of the dielectric constant in electrolytic dissociation, the dependence of the dielectric constant on the wave-length, and its relation to the structure of the dielectric, are discussed. J. F. S.

**The Electrostatic Potential of the Fluorspar Lattice.** ELISABETH BORMANN (*Zeitsch. Physik*, 1920, 1, 55—56).—An error in the calculation of the electrostatic potential of the fluorspar lattice, as given by A. Lande, has led to errors in later calculations of other authors in which this value was used. Thus the compressibility and the heat of formation of the crystal from the ions have been given erroneous values. These are corrected.

#### CHEMICAL ABSTRACTS.

**Activity-coefficient of Normal Potassium Chloride Solution and the Potential of the Normal Calomel Electrode.** JAMES A. BEATTIE (*J. Amer. Chem. Soc.*, 1920, 42, 1128—1131).—The *E.M.F.* of the cell  $\text{Ag, AgCl} | \text{KCl, } N | \text{KHg}_2 | \text{KCl } 0.1N | \text{AgCl, Ag}$  has been measured at  $25^{\circ}$ , and the value  $-0.10655$  (mean) obtained. Using this value, the activity ratio of *N*-potassium chloride to *N*/10-potassium chloride is found to be 0.7956. Using this value, the potential of the normal calomel electrode is  $E = -0.2700 + 0.5915 \log 0.592 \times 1.0328 = -0.2826$  volt, a value which is in agreement with that of Lewis, Sebastian, and Brighton (*A.*, 1918, ii, 25). The transport number of potassium in potassium chloride does not change much with dilution; the following values are obtained from the present work and that of MacInnes and Parker (*A.*, 1915, ii, 510): (1.0*N*—0.1*N*), 0.496; (0.5*N*—0.05*N*), 0.498; (0.1*N*—0.01*N*), 0.496; and (0.05*N*—0.005*N*), 0.494. J. F. S.

**Electrical Conductivity of Pure Salts in the Solid and Fused States. Determination of the Activity-coefficients of Ions in Solid Salts.** JNANENDRA CHANDRA GHOSH (*I.*, 1920, 117, 823—830).

**Free Energy of Dilution and the Transport Numbers of Lithium Chloride Solutions.** DUNCAN A. MACINNES and JAMES A. BEATTIE (*J. Amer. Chem. Soc.*, 1920, 42, 1117—1128).—The *E.M.F.* of cells of the type  $\text{Ag, AgCl} | \text{LiCl}(c_1) | \text{Li}(\text{Hg})_2 | \text{LiCl}(c_2) | \text{AgCl, Ag}$ , without a liquid junction, has been measured

at 25° for cells in which  $c_1$  and  $c_2$  varied between 3.0*N* and 0.001*N*, and a further series of *E.M.F.* measurements has been obtained for cells with liquid junctions of the type  $\text{Ag, AgCl} | \text{LiCl}(c_1) || \text{LiCl}(c_2) | \text{AgCl, Ag}$ . From the measurements, the activities of the ions and the degree of ionisation of lithium chloride have been calculated. The following values of  $\alpha$  have been obtained: 0.001*N*, 0.976; 0.003*N*, 0.962; 0.01*N*, 0.932; 0.03*N*, 0.899; 0.1*N*, 0.834; 0.3*N*, 0.759; 1.0*N*, 0.641; and 3.0*N*, 0.458. By combining the two sets of *E.M.F.* values, the transport numbers of the ions have been calculated, and, where possible, the values have been compared with the best values obtained by the Hittorf method. Since these numbers change rapidly with the concentration, a method has been devised by which the numbers can be calculated from the *E.M.F.* values and expressed as a function of the ion activity. In this way, the value of the transport number at any given concentration can be obtained. The following transport numbers of lithium in lithium chloride are obtained: 0.001*N*, 0.359; 0.005*N*, 0.341; 0.01*N*, 0.334; 0.02*N*, 0.327; 0.05*N*, 0.318; 0.10*N*, 0.311; 0.20*N*, 0.304; 0.30*N*, 0.299; 0.50*N*, 0.293; 1.0*N*, 0.286; 2.0*N*, 0.276; and 3.0*N*, 0.268.

J. F. S.

#### Electrochemical Behaviour of the Sulphates of Thallium.

G. GRUBE and A. HERMANN (*Zeitsch. Elektrochem.*, 1920, **26**, 291—297. Compare Abegg and Spencer, A., 1905, ii, 369).—The influence of the current density, acidity, and the anode material on the anodic formation of thallie sulphate in sulphuric acid solution has been investigated. It is shown that low current densities and a high acid concentration increase the current yield, and that a specific action of the anode material is active in the formation. The oxidation potential  $\text{Tl}^+/\text{Tl}^{++}$  in sulphuric acid solution has been re-measured, and the normal potential found to be  $\epsilon_A = +1.211$  volts. This value is independent of the acidity and the total concentration over a wide range. The difference between the value of Abegg and Spencer (*loc. cit.*),  $\epsilon_A = +1.156$ , and the present value is probably due to the liquid junction potential not being entirely accounted for in the earlier work. The potential obtained indicates that it is not possible to oxidise thallous sulphate to thallie sulphate in acid solution to a measurable extent by means of oxygen, and, for the same reason, thallous sulphate is unusable as a reaction accelerator of the oxygen electrode in an oxygen-hydrogen electrode with sulphuric acid as electrolyte. The potential of completely oxidised thallic sulphate solutions lies above that of the reversible oxygen potential. Consequently, it was possible to show that in such solutions, the potential of which was  $\epsilon_A = +1.26$  volts, the bubbling through of oxygen converted some of the thallic sulphate into thallous sulphate. This spontaneous reduction was accelerated by light and platinised platinum.

J. F. S.

The Critical State of Ethyl Ether. AUDANT (*Compt. rend.*, 1920, **170**, 1573—1575).—Using an optical method for studying



the critical opalescence and the variation of the critical temperature with the density of filling the tubes, the author obtains for ethyl ether the equation  $T_c = 190.22^\circ + 11D - 10D^2$ , where  $D$  is the density of filling. With rising temperature, opalescence commences  $0.5^\circ$  below  $T_c$  and finishes  $2.5^\circ$  above it, the same limits defining opalescence during cooling. The temperature of maximum opalescence is greater than  $T_c$ , and is higher the greater is the density of filling. The intensity of opalescence also increases with the density of filling.

W. G.

**Equation of State.** FRED. G. EDWARDS (*Chem. News*, 1920, 121, 3).—A theoretical paper in which equations are given for various quantities. It is stated that the molecular heat equation  $k = m^2 \log T$  may be converted into the equation of state,  $b(k + a \log \theta) = m^2 \log T$ , where  $\theta$  is the number of degrees below the critical temperature,  $a$  an infinitesimal coefficient producing the relative values of the intrinsic pressures at the critical and observational temperatures, respectively, and  $b$  is a constant making the sum in brackets equal to the intrinsic pressure, the surface tension, or the volume density with any given units. The values of  $y$  obtained from  $m = 5.95/y$  and  $m = 4 - (2y/2.95)$  will give the specific heats at variable volume, whilst  $m$  will be integral at the natural temperature of change of phase and recalescence. The specific density ratio,  $D = 1/m^2 \log T$ ; the coefficient of linear expansion,  $d \cdot V/3d \cdot T = 1/3d \cdot 1/4m^2 \cdot \log T = T/3.4m^2$ . The atomic volume ratio,  $V = 1/m^2 \log T$  is a more general form of the equation of Lother Meyer's curve,  $V = A/D$ .

J. F. S.

**Molecular Heat Equation.** FRED. G. EDWARDS (*Chem. News*, 1920, 120, 277—278).—A theoretical paper in which the author discusses the formula  $y = f(\log T - \log \theta)$ , in which  $\theta$  is the temperature at which  $y$  is one half the constant 5.95. The expression gives the relation between the entropies of different substances (Lewis and Gibson, A., 1918, ii, 29).

J. F. S.

**Entropy of Gases.** RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1920, 42, 1185—1193).—Making use of his theory of similitude (*Physical Rev.*, 1914, 3, 244; 4, 145; 1915, 6, 219; 1916, 8, 8; 1917, 9, 237), the author has deduced the expression  $S = 3/2R \log m + 5/2R \log T - R \log_e p + S_0$  as a general equation for giving the entropy of a gas,  $S_0 = 3/2R \log \alpha$ , and is a general constant independent of the gas. For constant temperature ( $298^\circ$  abs.) and constant pressure, the equation becomes  $S_{298} = 6.87 \log m + c$ , where  $c = 25.1$ . The entropy of mercury, cadmium, zinc, platinum, molybdenum, tungsten, helium, argon, hydrogen ( $H_2$ ), bromine, iodine, and hydrogen ( $H$ ) has been calculated by the above equation for 25° and 1 atm. pressure, and the values compared with the experimental values of Lewis and Gibson (A., 1918, ii, 29), and it is shown that where wide extrapolation is not necessary there is very good agreement between the calculated and experimental values. The least agreement is found in the

cases of molybdenum and tungsten, where extrapolation has to be made over  $1700^{\circ}$  and  $2100^{\circ}$  respectively; on the other hand, it is to be noted that in the case of platinum, where extrapolation extends over  $1500^{\circ}$ , there is a rather better agreement between the two values than in the case of hydrogen, where no extrapolation is necessary.

J. F. S.

**Modified Form of Freezing-point Apparatus.** O. MAASS (*Trans. Roy. Soc. Canada*, 1919, 13, iii, 97—99).—To prevent supercooling, a crystal of solid solvent is produced in the solution by the following device. A short piece of platinum wire is sealed through the tube at the side so as to be in contact with the solution. This projects outside the tube into a side-arm in the air jacket, the opening of which passes outside the cooling-bath through a side-neck. When supercooling begins, a small copper cylinder cooled in solid carbon dioxide is introduced through the side-arm and brought in contact with the platinum wire for a short time. A crystal forms on the tip of the wire in the solution. When the freezing point is determined a second time, it is possible to limit the supercooling to one-tenth of a degree.

J. R. P.

**Latent Heats of Vaporisation of Methane and Ethane.** JOHN SATTERLY and JOHN PATTERSON (*Trans. Roy. Soc. Canada*, 1919, 13, iii, 123—127).—Two methods were used. In the first, an electrically-heated wire evaporated some of the liquid, and in the second, a piece of copper was lowered into the liquid. In both cases, the evaporated hydrocarbon was collected over water. The heat supplied was calculated from the watts expended in the first case and the heat capacity of the copper in the second. The results (which are approximate) were: methane, 130 cal. per gram; ethane, 60 cal. per gram.

J. R. P.

**Heat of Sublimation and Valence Forces of Carbon Modifications.** K. FAJANS (*Zeitsch. Physik*, 1920, 1, 101—118. Compare this vol., ii, 354).—The heat of combustion of any aliphatic compound may be resolved into the following effects:  $nx$ , where  $x$  is the effect of breaking up of the union C-H and  $n$  is the number of such unions broken;  $nr$ ,  $r$  being the effect of the sub-reaction  $H + \frac{1}{2}O_2 = \frac{1}{2}H_2O$  and  $n$ , as before, the number of such sub-reactions;  $ny$ , where  $y$  is the heat effect of splitting the union C-C and  $n$  as before; and  $nz$ , where  $z$  is the effect of the reaction  $2 + O_2 = CO_2$ ,  $n$  as before. From a consideration of the heats of combustion, it is shown that the energy needed to break the single bond group C-C in a saturated hydrocarbon is the same as the energy needed to break up the same group in diamond, where all the atoms are the same distance apart and, therefore, held to each other with the same valence power. This energy is shown to have a value equal to one-half the heat of sublimation of diamond. This value of the heat of sublimation is calculated in two ways: (1) by the equation of Grüneisen; (2) from a consideration of the

change of temperature of the electric arc with the pressure, this temperature being the sublimation temperature of carbon. From the data of Lummer, the heat of sublimation is calculated with the aid of the Clapeyron equation. This value is corrected to that of the heat of sublimation of diamond. The value of the quantity  $y$  as given above may then be calculated, and the value of  $z$  is obtained from the equation  $z + 2y = C$ , where  $C$  is the heat of combustion of diamond. The value of  $v$  is calculated from yet other considerations, and the quantity  $x$  is then obtained from the equation  $-nx + nv - ny + nz = K = \text{heat of combustion of some aliphatic compound}$ . The values of these heat effects are as follows:  $x = -115,000$  cal.,  $y = -143,000$  cal.,  $v = 74,000$  cal.,  $z = 381,000$  cal. From these values, the heat of combustion of any aliphatic compound, for example, ethane, can be computed, thus:  $-(6 \times 115,000) + (6 \times 74,000) - 143,000 + (2 \times 381,000) = 373,000$  cal. The heat effects of splitting the groups  $C=C$  and  $C \equiv C$  can also be calculated. All values given are for  $20^\circ$ . It is also pointed out that, in spite of the difference in the arrangement of the atoms in diamond, graphite, and amorphous carbon, the total energy of the interatomic forces is within 1 or 2% of the same value.

CHEMICAL ABSTRACTS.

**Heat of Formation of Water.** W. A. ROTH (*Zeitsch. Elektrochem.*, 1920, **26**, 288—291).—A theoretical paper in which the various experimental data on the heat of formation of water are critically discussed, and, as a result, modified data are obtained, which are used to recalculate the heat of formation. The results obtained are: heat of formation from hydrogen and oxygen at  $18^\circ$  and under constant pressure is  $68.38$ ,  $15^\circ$  Cal., and at  $0^\circ$  the heat of formation of ice is  $69.96$ ,  $15^\circ$  Cal. The heat of fusion of ice per gram is  $79.67$ ,  $15^\circ$  Cal., and the molecular lowering of the freezing point is  $1.860^\circ$ .

J. F. S.

**Restatement and Correction of the Thermochemical Data on Organic Compounds. I. The Data of P. V. Zubov.** W. SWIENTOSLAWSKI (*J. Amer. Chem. Soc.*, 1920, **42**, 1092—1100).—In a previous publication (*A.*, 1918, ii, 32), the author advocates the use of naphthalene with a heat of combustion of  $9612$ ,  $15^\circ$  Cal., as a standard for determining the heat capacity of calorimetric bombs. In the present paper, the author has recalculated the whole of the thermochemical data of P. V. Zubov, obtained at Warsaw between 1892 and 1910 (compare *A.*, 1899, i, 589; 1902, ii, 188; 1904, ii, 159, 382; 1907, ii, 230; 1913, ii, 385, 830). The results for forty hydrocarbons, forty-one alcohols, twenty-three ketones, seven esters, nine acids, and six nitrogen compounds are given in tables, which include the heat of combustion of 1 gram of the substance weighed in air, the molecular heat of combustion ( $p$  or  $v$  const.), the molecular heat of the substance weighed in a vacuum, and the heats of combustion of the substances in the gaseous condition at constant pressure.

J. F. S.

**Heat of Adsorption of Vapours on Charcoal.** ARTHUR B. LAMB and A. SPRAGUE COOLIDGE (*J. Amer. Chem. Soc.*, 1920, **42**, 1146—1170).—The heat of adsorption by charcoal of the vapours of carbon tetrachloride, diethyl ether, chloroform, ethyl formate, carbon disulphide, methyl alcohol, ethyl chloride, ethyl bromide, ethyl iodide, benzene, and ethyl alcohol has been determined at 0° over a considerable range. The resulting values are shown to be reproducible and independent of the rate of adsorption of the vapour and of the previous history of the charcoal. The heat of adsorption in all cases can be represented very precisely as a function of the amount adsorbed by the expression  $h = mx^n$ , where  $h$  is the heat of adsorption per normal c.c. of vapour,  $x$  the number of c.c. of vapour adsorbed, and  $m$  and  $n$  constants which are characteristic of the vapour. The constant  $n$  is found to be very nearly unity. The heat of adsorption, therefore, decreases but slightly with increasing amount of adsorption. In other words, there is but slight evidence of fatigue in the adsorptive forces. It has been shown that this decrease, represented by  $1-n$ , is antitab to the boiling points of the liquids; that is, the liquids with relatively high boiling points exhibit a small value for  $1-n$ , and hence a slight fatigue. This is due to the fact that such liquids have a high latent heat of vaporisation. The constant  $m$  also varies relatively little from vapour to vapour. In general,  $m$  and  $n$  tend to vary in opposite directions. In agreement with this, the actual molecular heats of adsorption of the various liquids measured are not very different, varying between 12.0 cal. for ethyl chloride and 15.5 cal. for carbon tetrachloride. The heats of adsorption of these vapours are very nearly the same on inactive as on active charcoal of the same kind. Vapours containing halogens appear to react with the charcoal when warmed, so as to decrease the heat developed by any subsequent adsorption of gas, without, however, greatly affecting the fatigue effect. The net heats of adsorption, that is, the heats developed above those corresponding with the latent heats of vaporisation, are approximately of the same magnitude as the latent heats of vaporisation, and the net heats of adsorption per c.c. of liquid are very nearly identical for all the liquids studied. The net heats of adsorption are closely proportional to the heats of compression under high pressure. This indicates that the liquids are all attracted by the charcoal with substantially the same force, and that the net heat of adsorption is merely a heat of compression. The absolute value of this attractive force appears to be about 37,000 atmospheres where 1 c.c. of liquid is adsorbed on 10 grams of charcoal. The molecular adsorbability, that is, the number of c.c. of gas adsorbed at a fixed gas pressure (20 mm.), is inversely proportional to the molecular volume of the liquid. The molecular adsorbability is inversely proportional to the net molecular heat of adsorption. This regularity follows from the previously mentioned regularities. All the above evidence indicates that the liquid films studied are at least one, and usually very many molecules thick, and this is

confirmed by a consideration of the actual volume occupied by the liquid and the approximately known capillary volume and surface of the charcoal. J. F. S.

**"Vapour Density" a Misnomer.** PHILIP BLACKMAN (*Chem. News*, 1920, 120, 592).—The author maintains that the term vapour density is incorrect for the quantities usually called by this name; these are in reality vapour specific gravities. The term vapour density should be used for the weight of unit volume of a gas or vapour under standard conditions. J. F. S.

**Variation of the Coefficient of Viscosity of Gases with Temperature.** ROBERT CLARK (*Trans. Roy. Soc. Canada*, 1919, 13, iii, 177—180).—If two vessels of known volumes be connected by a capillary tube, any pressure difference between them will gradually disappear, owing to flow through the capillary. This flow can be calculated in terms of the rate of change of pressure difference and the volumes of the two vessels; from the dimensions of the capillary tube, the coefficient of viscosity may be determined. If the rate of change of pressure be observed when the apparatus is maintained at different temperatures, the values of the coefficient of viscosity corresponding with these temperatures may be obtained. The viscosities of carbon dioxide, hydrogen, and dry air at temperatures between 0° and 110° were determined, and the value of the coefficient  $n$  in the equation  $\mu = \mu_0(T/273.1)^n$  found to be: air, 0.750; carbon dioxide, 0.965; hydrogen, 0.700. The viscosity of air at 23.0° was found to be  $184.0 \times 10^{-6}$ . J. R. P.

**The Effect of the Addition of certain Fatty Acids on the Interfacial Tension between B.P. Paraffin Oil and Mercury.** SHANTI SWARUPA BHATNAGAR and WILLIAM EDWARD GARNER (*J. Soc. Chem. Ind.*, 1920, 39, 185—187t. Compare Wells and Southcombe, *Ibid.*, 51t).—The measurements of interfacial tension between the oil and mercury were made by the dropping pipette method, as described by Donnan (*A.*, 1900, ii, 201). The four acids used were oleic, stearic, linolic, and palmitic acids, and curves are given showing the surface tensions of solutions of varying concentrations of these acids in B.P. paraffin oil. The curve for oleic acid shows a point of inflexion at a concentration of about 0.5%. The curves for oleic, stearic, and palmitic acids are very similar in character, especially at the higher concentrations, but the surface tensions of the linolic acid solutions are much lower than those of the corresponding solutions of the other three acids. The curves obtained are very similar to those given by Langmuir for fatty acids (*A.*, 1917, ii, 525), and, applying Langmuir's views, it would appear that the increased efficiency as a lubricant of a mineral oil to which an organic acid is added runs parallel with a lowering of tension at the metal oil interface. W. G.

**Density of Adsorbing Materials.** STUART MCLEAN (*Trans. Roy. Soc. Canada*, 1919, 13, iii, 197—199).—The density of

materials was found by the volumenometer method, using helium as the filling gas, since it is not adsorbed at ordinary temperature. The following mean results were found: coconut charcoal (heated to  $400^{\circ}$ ), 1.53; lignite carbonised at  $350^{\circ}$ , 1.33; lignite carbonised at  $450^{\circ}$ , 1.46; lignite carbonised at  $550^{\circ}$ , 1.44.

J. R. P.

**Properties of Wood Charcoal.** ALWYN PICKLES (*Chem. News*, 1920, 120, 301—302).—It is shown that coconut charcoal, prepared by heating at  $900^{\circ}$ , becomes more efficient towards a gas on keeping for some time in the air; this may be due to sorption of water, but it is also due to a spontaneous disintegration of the charcoal. Prolonged heating increases the efficiency of the charcoal, and treatment with acid removes sulphur as hydrogen sulphide and prevents friability. Birch charcoal is a more efficient absorber of colouring matter than animal charcoal, and since its density (1.46) is about one half that of animal charcoal, mechanical stirring is not required to the same extent. The adsorption of water from solutions of alkali haloids (negative adsorption) has been investigated at various temperatures. It is shown that at  $40^{\circ}$  the negative adsorption suddenly increases, and it is at this temperature that the interior of the charcoal is becoming opened out by the solvent action of the solution. It is very probable that the first removal of the water from the solution is due to the surface effect of the charcoal (true adsorption) and that as the temperature rises this effect diminishes with the decreasing surface tension of the water. The interior, or absorption, effect, however, continues to increase and speedily more than counterbalances the decreasing surface effect.

The following types of substances are negatively adsorbed from aqueous solutions: (i) those of simple structure; (ii) highly ionised substances; (iii) compounds with a strongly electropositive cation; (iv) compounds with a univalent metallic cation; (v) compounds having ions with a high mobility.

J. F. S.

**Effect of Pressure on Gas Adsorption.** ALWYN PICKLES (*Chem. News*, 1920, 121, 1—2).—Equal volumes of charcoal (50 c.c.) from birch chips, coconut, fruit-stone dust, palm nut, almond, and birch dust were rendered free from air by heating and saturated with ammonia at ordinary pressure and temperature. They were then placed individually in an air-tight glass vessel fitted with a manometer and an aspirator tube, and the pressure reduced to a measured point. The apparatus was closed and the change of pressure with time observed. The initial pressures were about 20, 40, and 60 cm. In all cases the pressure at first increased, and eventually (one to two hours) decreased, but in no case was the initial pressure regained. The first effect of aspiration is to remove the gas on the charcoal surface, then gas escapes from the interior, and so increases the pressure, the subsequent decrease being due to surface condensation. The results give an indication of the inner structure of the charcoal. Where a rapid increase of pressure occurred, a complex internal structure may be

assumed (coconut and fruit-stone charcoal). In the case of birch dust, the gas-adsorbing capacity is mainly a surface effect. Palm-nut charcoal was used in large pieces, and it retained the gas mainly by absorption. The apparent density,  $AD$ , and the true density,  $D$ , have been determined for each variety used, and the following values obtained: almond,  $AD$  0.48,  $D$  1.70; birch chips,  $AD$  0.23,  $D$  1.44; fruit stone,  $AD$  0.68,  $D$  1.72; birch dust,  $AD$  0.21,  $D$  1.47; coconut,  $AD$  0.63,  $D$  1.71; and palm nut,  $AD$  0.64,  $D$  1.59. The carbon content of all varieties was about 85%. The porosity of charcoal dust is increased by mixing it with solid ammonium dichromate and heating out of contact with air. In this way, the gas-adsorbing efficiency per c.c. of actual charcoal is increased, but per c.c. of the whole product it is decreased. As gas adsorbents, the denser charcoals are the most efficient; the order of efficiency is palm nut, coconut, fruit stone. J. F. S.

**Adsorption of Gases by Carbonised Lignites.** STUART McLEAN (*Trans. Roy. Soc. Canada*, 1919, 13, iii, 187—199).—The adsorption of air, carbon dioxide, oxygen, hydrogen, and nitrogen by lignite was studied. Oxygen is adsorbed much more readily than nitrogen. The presence of water vapour decreases the amount of gas adsorbed. No permanent adsorption takes place, since there are but few cases where the last weight is greater than the first, and these may be due to experimental error. Chemical action may be taking place in the case of oxygen. The fact that in most cases the last weight is less than the first indicates that the oxygen combines with the lignite, forming carbon dioxide, which is given off when the lignite is heated, making the sample lighter.

J. R. P.

**Velocity of Sorption.** ALWYN PICKLES (*Chem. News*, 1920, 121, 25—27).—The sorption by charcoal of benzoic acid from alcohol solution at 14°, iodine from  $N/10$ -potassium iodide solution at 15°, 25°, 50°, and 70°, and potassium permanganate in  $N/10$ -concentration from water at 12°, 25°, 50°, and 70°, has been determined with respect to the velocity with which these substances are taken up. It is shown that, on applying the equation for unimolecular reactions to these cases, a "constant" is obtained which continually decreases, but by using the equations

$$K = 1/t \log_e a/(a-x) - 0.4343x/a$$

and  $K = 1/(t_2 - t_1) \log_e (a - x_1)/(a - x_2) - 0.4343(x_2 - x_1)/a$  a very fair constant is obtained in the case of iodine and benzoic acid, whilst very irregular values are obtained for permanganate. These are attributed to catalytic decomposition of the permanganate by the charcoal, solvent action of the solution in opening up the charcoal capillaries, and the reducing effect of the charcoal. In all the above cases birch-dust charcoal was used.

The velocity of sorption of ammonia and hydrogen chloride by coconut charcoal has been determined at 13°. In the case of ammonia, the "constant" of the unimolecular equation falls steadily with time, but the equations mentioned above give a good

constant. With hydrogen chloride, the "constant" of the unimolecular reaction gives a moderately good constant, but the value of  $K$  increases rapidly with time, which seems to show that the hydrogen chloride is continually opening up fresh surfaces.

J. F. S.

**The Absorption of Colouring Matters by Charcoal.**

EDMUND KNECHT (*J. Soc. Dyers and Col.*, 1920, **36**, 201).—Knecht replies to the statement by Philip, Dunnill, and Workman (T., 1920, **117**, 302) that Knecht and Hibbert (*J. Soc. Dyers and Col.*, 1916, **32**, 226) correlate the activity of a charcoal in decolorising solution with its nitrogen content, and shows their original contention to be that whilst for a basic dye, such as methylene-blue, the nitrogen content does not affect the absorptive power, for an acid colour, such as crystal-scarlet, the absorptive power of an animal charcoal is in proportion to its fixed nitrogen content. This contention has not yet been controverted. Knecht still regards the absorption of methylene-blue as being connected with the oxygen content of the charcoal.

A. J. H.

**The Deliquescence and Drying of Ammonium and Alkali Nitrates and a Theory of the Absorption of Water Vapour by Mixed Salts.**

E. B. R. PRIDEAUX (*J. Soc. Chem. Ind.*, 1920, **39**, 182—185r).—The author has measured the vapour pressures of saturated solutions of ammonium nitrate, potassium nitrate, and of a solution saturated with ammonium nitrate and sodium nitrate. The results of the latter determinations show the added difficulty of drying an impure salt, and also, if such has to be dried, that raising the temperature is not necessarily and in all cases advantageous. If the ratio, relative humidity of salt to relative humidity of air, is greater than 1, drying is possible, and the speed of drying could probably be expressed by the van't Hoff maximum work expression,  $4.577 \log p_1/p$  for 18 grams of water, where  $p_1$  is the pressure of water vapour in the atmosphere and  $p$  is the pressure of water vapour in equilibrium with the univariant system, salt-saturated solution-vapour, at a given temperature.

The gains in weight of sodium nitrate plus varying amounts of sodium chloride in atmospheres of different humidities have been measured. The manner in which deliquescence occurs in a mixture of soluble salts is discussed, and it is considered that such deliquescence takes place in two stages.

W. G.

**The Adsorption Capacity of Cellulose. Remarks about the Electrometrical Micro-analysis of Chlorine.**

P. RONA and L. MICHAELIS (*Biochem. Zeitsch.*, 1920, **103**, 19—30).—Cellulose does not appreciably adsorb surface-active non-electrolytes. Only in the case of extremely surface-active substances can very slight adsorption be established. The more marked adsorption of dyes by cellulose is due to the ash content of the cellulose.

The estimation of chlorine by the electrical method with a calomel electrode is described and discussed.

S. S. Z.



**The Condition of Dissociation of Ampholytes. I. The Influence of Univalent Ions Disregarding all Colloidal Phenomena.** L. MICHAELIS (*Biochem. Zeitsch.*, 1920, 103, 225—243).—A theoretical discussion of the influence of ions on the dissociation of acids, bases, and ampholytes, for which they have a chemical affinity. S. S. Z.

**Process of Diffusion Through a Rubber Membrane.** H. A. DAYNES (*Proc. Roy. Soc.*, 1920, [A], 97, 286—307).—The diffusion of hydrogen, nitrogen, oxygen, carbon dioxide, nitrous oxide, and ammonia through rubber sheets has been examined by means of the katharometer (this vol., ii, 503). It is shown that the behaviour of a set of rubber films agrees in all respects, within the limit of the experiments, with that predicted from assumptions of a simple process of diffusion through a rubber membrane. The conclusion previously reached, that the surface resistance is negligible, is thus confirmed. The method furnishes a rapid and satisfactory means of measuring the absorption and the diffusion constant of a material for a gas, and is capable of a high degree of precision. The mean value of the diffusion constant for the three films examined was  $11.4 \times 10^{-6}$  cm./sec. at  $20^\circ$ , the actual values being  $11.7 \times 10^{-6}$ ,  $10.4 \times 10^{-6}$ , and  $13.6 \times 10^{-6}$  cm./sec. The mean value of the absorption coefficient was 0.035 at normal pressure and  $20^\circ$ , the actual values being 0.035, 0.037, and 0.031. The coefficient of absorption has a low temperature-coefficient, approximately 0.5%/1°, compared with that of the diffusion constant. It is not that which is responsible for the great variation of permeability with temperature. This suggests that the process of absorption is a simple molecular action. J. F. S.

**The Cause of the Influence of Ions on the Rate of Diffusion of Water Through Collodion Membranes. II** JACQUES LOEB (*J. gen. Physiol.*, 1920, 2, 563—576).—The effect of ions carrying charges of different signs on the free osmosis of water through a collodion membrane which separates it from a solution of an electrolyte has been discussed previously (compare this vol., ii, 94, 233, 234). It is now shown that the influence of the concentration of electrolytes on the rate of transport of water through collodion membranes in electrical endosmosis is similar to that in the case of free osmosis.

On the basis of Helmholtz's theory of electrical double layers, this influence of an electrolyte on the rate of diffusion of water through a collodion membrane is due to the ions increasing or decreasing the density of charge on the membrane. The relative influence of the oppositely charged ions on this density is not the same in all concentrations. The influence of the ion with the same sign of charge increases in the lowest concentrations more rapidly with increasing concentration than the influence of the ion with the opposite sign of charge, whilst for somewhat higher concentrations the reverse is true. W. G.

**The Reversal of the Sign of the Charge of Membranes by Hydrogen Ions.** JACQUES LOEB (*J. gen. Physiol.*, 1920, 2, 577—594).—When a collodion membrane is treated with a protein, the membrane assumes a positive charge when the hydrogen-ion concentration of the solution with which it is in contact exceeds a certain limit (compare preceding abstract). By this treatment, a thin film of protein adheres to the membrane, and the positive charge of the membrane is localised in this protein film. The hydrogen-ion concentration at which the reversal in the sign of the charge of a collodion membrane treated with a protein occurs varies in the same sense as the isoelectric point of the protein with which the membrane has been treated, and is always slightly higher than that of the isoelectric point of the protein used. Thus the critical hydrogen-ion concentration required for the reversal appears to be that concentration where enough of the protein lining of the membrane is converted into a protein-acid salt, for example, gelatin nitrate, capable of ionising into a positive protein ion and the anion of the acid used.

W. G.

**Atomic Structure and Crystal Symmetry.** HANS THIRRING (*Physikal. Zeitsch.*, 1920, 21, 281—288).—A theoretical paper in which the symmetry of crystals, particularly that of the diamond and sylvine, is considered. Since the reflexion of Röntgen rays from the lattice surface of a crystal depends only on the number of electrons per unit surface, and is independent of the orientation of the atoms, account must be taken of the possibility that the length of edge of the elementary cube of the atom lattice is an integral multiple of that of the corresponding point lattice. This multiple is represented by  $n$ , and, taking account of this possibility, the following points are deduced: The carbon atom cannot possess a cylindrical symmetry, that is, it has not a Bohr single-plane system of electrons. Systems with crossed electron rings cannot be brought into line with the symmetry of the diamond; on the other hand, those systems to which Landé attributes a tetrahedral symmetry may be brought into line with the diamond symmetry. The explanation given by Bragg ("X-Rays and Crystal Structure," p. 158) for the hemihedrism of potassium chloride, namely, that the atoms do not occupy exactly the corners of the cube or the middle points of the surfaces, but positions a little removed from them, must be abandoned, because this explanation leads to the value  $n=2$ , which does not agree with any equilibrium position. It is not possible to construct a regular enantiomorphic symmetry for potassium chloride from axial symmetric atoms so long as the assumption is maintained that no potassium or chlorine atom is different from the others. Using Landé's atom model, the hemihedrism of potassium chloride can be explained by  $n>2$  if it is assumed that the magnetic forces set up by the potassium atom play an important part in the properties of the symmetry of the crystal. From the holohedrism of sodium chloride, it follows that the magnetic forces of the alkali metals decrease down the periodic system group in the sense that

they are unnoticeable in the case of sodium, but in the case of potassium they exercise an influence on the crystal symmetry.

J. F. S.

**Crystallisation of Supersaturated Solutions and Supercooled Liquids.** D. McINTOSH (*Trans. Roy. Soc. Canada*, 1919, 13, iii, 265—272).—The sizes of particles of solid which induce crystallisation of supersaturated sodium sulphate solution and supercooled salol were found to be: sodium sulphate,  $10^{-13}$  to  $10^{-18}$  gram in one method,  $10^{-12}$  to  $10^{-14}$  gram in another; salol,  $10^{-9}$  gram to  $4 \times 10^{-15}$  gram. These are much below the numbers formerly accepted.

J. R. P.

**Periodic Precipitation. I. Silver Chromate in Gelatin.** ALEXANDER MITCHELL WILLIAMS and MARY RUSSELL MACKENZIE (*T.*, 1920, 117, 844—852).

**Composition of the Vapour and Liquid Phases of the System Methane-Nitrogen.** H. A. McTAGGART and E. EDWARDS (*Trans. Roy. Soc. Canada*, 1919, 13, iii, 57—66).—The temperature-composition diagram for the system methane-nitrogen at atmospheric pressure was obtained, and the constants in the formula  $\log r' = a + b \log r$ , where  $r$  = ratio methane/nitrogen in liquid, and  $r'$  the corresponding ratio in the vapour, determined as  $a = -0.47$ ,  $b = +0.85$ .

J. R. P.

**Velocity of Reactions.** M. POLANYI (*Zeitsch. Elektrochem.*, 1920, 26, 228—231).—A theoretical paper in which certain difficulties in the deduction of the equations for the velocities of reactions are discussed (compare Herzfeld, A., 1919, ii, 503; Polanyi, this vol., ii, 238).

J. F. S.

**Reaction Isochore and Velocity of Reaction from the Statistical Point of View.** M. POLANYI (*Zeitsch. Elektrochem.*, 1920, 26, 231).—A correction of some of the mathematical expressions in a previous paper (this vol., ii, 238).

J. F. S.

**The Ignition of Gases. I. Ignition by the Impulsive Electrical Discharge. Mixtures of Methane and Air.** RICHARD VERNON WHEELER (*T.*, 1920, 117, 903—917).

**Colloidal Solutions and Organic Syntheses. II. Mechanism of the Synthesis of Nitrobenzylidene Diacetate.** M. BAKUNIN and F. GIORDANI (*Rend. Acad. Sci. Fis. Mat. Napoli*, 1917, [iii], 23, 39—50. Compare A., 1916, ii, 421).—The authors have investigated the equilibrium of the reaction,  

$$(\text{CH}_3\text{CO})_2\text{O} + \text{NO}_2\text{C}_6\text{H}_4\text{CHO} \rightleftharpoons \text{NO}_2\text{C}_6\text{H}_4\text{CH}(\text{OAc})_2$$
both without solvent and in ethereal solution, with the object of deducing the heat of the reaction by means of van't Hoff's equation,  $d \log K / dT = -Q / RT^2$ .

The results of the experiments with *p*-nitrobenzaldehyde and

acetic anhydride in ethereal solution, and in presence of ferric oxide or phosphoric oxide, show that these oxides merely alter the velocity with which the condition of equilibrium is reached, the reaction being thus catalytic.

The reactions without solvent were carried out in presence of a colloidal solution of phosphoric oxide in acetic anhydride; here, too, the results show that this condensing agent acts purely catalytically. The value of  $Q$  is 3·911 cal. and 9·247 cal. for the reactions with *o*- and *p*-nitrobenzaldehyde respectively. With the meta-compound, the solubility in acetic anhydride is very slight at low temperatures, and the values of the reaction constant obtained at higher temperatures are of about the same order of magnitude as the experimental error.

The probable mechanism of the action of colloidal solutions in these reactions is discussed (compare Duclaux, A., 1911, ii, 479; de Hemptinne, A., 1904, ii, 224; Burton, A., 1906, ii, 275; Perrin, A., 1905, ii, 138).

T. H. P.

**The Catalytic Decomposition of Hydrogen Peroxide by Colloidal Platinum.** A. DE GREGORIO ROCASOLANO (*Compt. rend.*, 1920, 170, 1502—1504).—Contrary to the conclusion of Bredig, it is shown that when electrosols of platinum are used, the decomposition of hydrogen peroxide by colloidal platinum is not a unimolecular reaction. During the reaction, the catalyst itself apparently undergoes some change. This altered catalyst will decompose further quantities of the peroxide, and the reaction is then unimolecular.

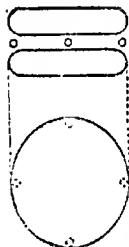
W. G.

**Annual Report of the International Committee on Atomic Weights for 1920–1921** (T., 1920, 117, 885—888).

**The Nuclei of Atoms and the New Periodic System.** WILLIAM D. HARKINS (*Physical Rev.*, 1920, 15, 73—94).—A

summary and extension of previous papers on the nuclear structure of atoms. The data on which any theory of nuclear structure are based are atomic masses, atomic numbers which are assumed to be equal to nuclear charges, and atomic stabilities (given by the periods of disintegration when the atoms are radioactive), supposed by the author to be related to the relative abundance of the atomic species (elements) in nature. From these data, it is assumed (1) that all nuclei consist of positive electrons (or hydrogen nuclei= $\eta^+$ ) or  $\alpha$  particles, and negative electrons ( $\beta^-$ ). Almost all of these are grouped in  $\alpha^{++}$  particles or helium nuclei= $\eta_4^+\beta_2^-$ ; a few are grouped as  $\mu\mu$  particles ( $\mu=\eta_3^+\beta_2^-$ ), both of which carry an even net charge; and a few as  $\mu\nu$  particles [ $\nu=(\eta_3^+\beta_2^-)^+$ ], which have an odd charge, and are responsible for the existence of most atoms of odd atomic number, which are relatively rare. Thus, negative electrons almost always occur in pairs as binding electrons in these primary groups. Also pairs of cementing electrons are present in all heavy nuclei where they are

used to attach extra  $\alpha$ -particles. Only the cementing electrons are given off in the disintegration of radio-atoms. The atomic weights indicate that chlorine, silicon, magnesium, neon, copper, zinc, nickel, and all elements with numbers from 28 to 80 (Hg), consist of mixtures of isotopes. All atomic weights of atomic species are approximately whole numbers, with the exception of hydrogen, which has the weight 1.0078. These whole numbers are given by the Harkins-Wilson equation,  $W = 2(N + n) + \frac{1}{2} + \frac{1}{2}(-1)^{N-1}$ , where  $n$  is the number of cementing electrons in the nucleus, and varies in steps of 2 up to 26, which is the maximum. Using this equation, Durrant showed the normal plot for the cementing electron content of atoms. A simpler equation is  $W = 2(N + n)$ . Equations are also given for the number of  $\alpha$ -particles and cementing electrons in the nucleus. The atomic weight of the  $\alpha$ -particle in complex nuclei is 4.000, as nearly as can now be told. If any atomic weights, except that of hydrogen, are not integers, it is only the atomic weights of the radioactive elements which deviate, and these may possibly be slightly higher than the corresponding whole numbers. The  $\alpha$ -particle is assumed to consist of four positive electrons at the corners of a square lying in a plane, with one negative binding electron above and one below the plane.



The negative electrons are, with Rutherford, assumed to be relatively large, so that each one is close to all four positive electrons. This structure (see fig.) is assumed to be responsible for the difference in weight between the positive electrons and the  $\alpha$ -particle. Nearly all elements are mixtures, so the term "atomic species" is proposed to indicate all atoms of one composition and structure. It is only the atomic weights of the atomic species which are whole numbers, since most of the mixtures (elements) are not in the proper proportion to give this result. An element may have an integer for an atomic weight if (1) it

consists of one species, or (2) when only one isotope has a sufficient stability to make it evident in the atomic weights. The former is probably the case with such light atoms as oxygen, whilst the latter is true of the radioactive elements. Between atomic numbers 82 and 10 (possibly below this), is the region of stable isotopes. Two classes of isomeric atoms exist. (1) Non-isotopic isomerides, as  $UX_1$ ,  $UX_2$ , and  $U_2$ , or  $\alpha_{74}\mu\beta_{21}e'_{46}e_4$ ,  $\alpha_{78}\mu\beta_{25}e'_{46}e_5$ , and  $\alpha_{88}\mu\beta_{34}e'_{86}e_6$ , and (2) isotopic isomerides, which have the same nuclear composition. Here  $e$  represents a valence, and  $e'$  a non-valence planetary electron. Of the ordinary atoms, calcium and argon are isomeric, the difference in structure being due to the inclusion of two cementing electrons in the argon nucleus, which in calcium are present in the planetary system of non-nuclear electrons. The formulae for the composition of the first twenty-seven elements and the radioactive elements are given, and it is possible to express radioactive changes by equations. Thus,  $\alpha_{80}\mu\beta_{26}e'_{86}e_6$  is the

formula for uranium,  $\alpha_{55}\beta_{28}e'_{86}e_4$  for thorium,  $\alpha_{51}\mu\beta_{20}e'_{78}e_4$  for radio-lead, and  $\alpha_{52}\beta_{22}e'_{76}e_4$  for thorium-lead. An alpha change is then indicated by the equation  $\alpha_{55}\beta_{28}e'_{86}e_4 \rightarrow \alpha_{57}\beta_{20}e'_{86}e_2 + \alpha^{++} + 2e^-$  (Th to meso-Th'), whilst a beta change is of the type  $\alpha_{55}\mu\beta_{23}e'_{78}e_5 + e^- \rightarrow \alpha_{53}\mu\beta_{22}e'_{76}e_6 + \beta^-$  (Ra-C to Ra-C'). In the nuclear structure of the light elements, the  $\nu$ -group ( $\eta_3\beta_2$ ) occurs frequently, and is characteristic of the odd-numbered elements. Experiments proving that chlorine is a mixture of isotopes are nearing completion. These consist in a separation of chlorine into a lighter and a heavier fraction by diffusion.

## CHEMICAL ABSTRACTS.

**Electrons and Chemical Potential.** FRED G. EDWARDS (*Chem. News*, 1920, 120, 292—293).—A discussion of some points put forward by Henri (*Etudes de Photochimie*, Gauthier-Villars, Paris). The author derives the following statements from Henri's work. (1) Given the true graphic formula of any compound, the single bond represents one electron between the respective atoms. (2) The double bond appears when this single electron is withdrawn. The characteristic vibration is displaced towards the infrared by the consequent increase of mass in the vibrator, changing the speed of propagation and consequently the angle of dispersion. The three double bonds usually shown for benzene do not exist. (3) A triple bond appears when a second electron is similarly removed from the same pair of atoms. (4) A complete wave-length of incident light reciprocating with one electron of a molecule constitutes reciprocal absorption and emission. (5) An infra-red half-wave-length ( $E=h\nu$ ) absorbed by a molecule represents the addition of one electron. (6) An ultra-violet half-wave-length ( $E_1=h\nu_1$ ) absorbed represents the motion of an electron the distance of half a wave-length from one position in the molecule to another, and provides the mechanism of tautomerism. (7) There is a similar number of ultra-violet bands, the respective frequency of which is a large integral multiple of every respective infra-red band, the latter representing the total removal or replacement of an electron, but the former merely a rearrangement of its position in the molecule.

J. F. S.

**An Electronic Theory of Isomerism.** W. E. GARNER (*Nature*, 1920, 104, 661—662).—The theory differentiates between two kinds of valency, according as the rotation of the electrons with respect to the valency is clockwise or anti-clockwise. Various types of isomerism (for example, eight possible isomerides of cinnamic acid) are discussed on the basis of this theory. All the isomerides, except the optical pairs, should possess different free energies, according to the arrangement of the rotating electrons.

J. R. P.

**Space Filling and Ionic Mobility.** RICHARD LORENZ (*Zeitsch. Elektrochem.*, 1920, 26, 221—228).—A theoretical paper, in which

the relationships between the filling of space by the molecules and the ionic mobility are discussed. It is shown from these relationships that the mobility may be calculated within limits from the space filling. This calculation is based on Stokes's formula applied to large ions, and it gives values for the molecular radii which are of the correct order of magnitude. The molecular volume of the ions obtained in this way is compared with the molecular volume of the ion substance, and in the majority of cases it is found that the molecular volume of the ions ( $\phi$ ) is smaller than the molecular volume of the ion substance ( $V_0$ ). The term space-filling ( $\psi$ ) is defined as the ratio of the space occupied by the molecules to that occupied by the mass of substance, and for the purpose of obtaining comparable results the last-named quantity is referred to absolute zero. The ratio is expressed by  $\psi = \phi/V_0$ . The space-filling figures can be calculated from the different theories of the equations of condition. The results are tabulated. Since the equations of condition are not absolutely definite, the space-filling is obtained as a value between two extremes,  $0.74 > \psi > 0.25$ . The space-filling values calculated from the ionic mobility all lie between these two extremes. A table of values is given which includes those for sixty univalent organic cations, thirty-seven univalent organic anions, six bivalent organic cations, and thirteen complex inorganic salts. This relationship constitutes electroconductivity as a branch of experimental atomistics. The experimental space-filling values correspond approximately with the space-filling in cubic packing. The equations of condition of Sutherland and Reinganum correspond most closely with the requirements of the present work. The  $\psi$ -curves obtained are shown to represent a first approximation only. Ions with normal space-filling numbers cannot be hydrated. J. F. S.

**Theory of Electrolytic Ions. XV. Space-filling and the Mobility of Univalent Organic Anions.** RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1920, **111**, 148-150. Compare A., 1919, ii, 212, 262, 264; this vol., ii, 410).—The univalent organic anions bear a different relationship between the space filling and the mobility than do the cations (*loc. cit.*). The volume of the ion substance ( $V_0$ ) is analogous to that in the case of the cations;  $V_0 = \sigma \times z$ , where  $\sigma$  is the stere (5.75) and  $z$  is the number of atoms in the ion. The molecular volume of the ion  $\phi$ , and the volume of the ion substance  $V_0$ , give the space-filling numbers  $\psi$ , according to the equation  $\phi/V_0 = \psi$ . J. F. S.

**Structure of Matter and the Quantum Theory.** F. H. LORING (*Chem. News*, 1920, **120**, 291; **121**, 2-3).—Supplementary notes to the author's previous paper (this vol., ii, 365). The table previously given is completed up to, and including, nickel. J. F. S.

**Experiments with a New Micro-balance.** HANS PETTERSSON (*Proc. Physical Soc.*, 1920, **32**, 209-221).—The balance is wholly

of quartz, the usual knife-edge support being replaced by a pair of quartz fibres. Magnetic arrestment is employed, and balance obtained by displacement of a bulb at different pressures of air or magnetically. The range of weighings depends on the size of the beam; with one 5 cm. in length, the maximum load is 100–200 mg., and the setting can be made to within  $10^{-7}$  mg.

J. R. P.

**Use of Acetylene as a Source of Heat in Chemical Laboratories.** NAUMANN (*Zeitsch. angew. Chem.*, 1920, **33**, i, 148).—Acetylene is readily generated from calcium carbide, and when burnt in a specially constructed Bunsen burner yields a very hot, non-luminous flame.

W. P. S.

**Explosion Accident at the Chemical Institute, University of Munster i.W., and Its Cause.** R. SCHENCK (*Zeitsch. angew. Chem.*, 1920, **33**, ii, 245; *Chem. Zeit.*, 1920, **44**, 497).—During a lecture experiment to show combustion by combined oxygen, in which a mixture of toluene and tetranitromethane was being burnt, a violent explosion occurred, by which some thirty people were more or less injured. The cause of the explosion lay in the faulty preparation of the mixture. The correct quantities for safe burning are 67.5 c.c. of tetranitromethane (D 1.65) and 7.5 c.c. of toluene (D 0.8), but in place of this 67.5 grams of tetranitromethane and 7.5 grams of toluene had been taken, that is, the relative proportion of toluene was doubled.

J. F. S.

## Inorganic Chemistry.

**Reaction between Hydrogen Peroxide and Peracids.** A. RICS Y MIRÓ (*Anal. Fis. Quim.*, 1920, **18**, 35–42).—It is shown that hydrogen peroxide, previously proposed as a reagent for hydroperoxides (this vol., ii, 368), reduces peracids of the types  $RO_2R$  and  $RO_2H$ . The author repeated the experiments of Riesenfeld (A., 1905, ii, 825; 1909, i, 263; ii, 951; 1910, ii, 51), according to whom perchromic acid has the formula  $H_2CrO_5$ ; but, instead of 5 mols. of oxygen evolved per mol. of dichromate (thus,  $2CrO_4^{IV} + 12H^+ = 2Cr^{III} + 6H_2O + 5O_2$ ), he found 4.6 to 6.5, which he explains by assuming the formation of Caro's acid. The author did not measure the evolved oxygen, but determined the amount of undecomposed hydrogen peroxide with permanganate, after adding the dichromate through a burette to the mechanically agitated acid solution of hydrogen peroxide. The oxygen evolved was found to be 3.71 to 4.33 mols. per mol. of dichromate. The greater evolution of oxygen corresponded with a low acidity,



because peracids are hydrolysed in acid solutions. The highest values must be due to the formation of an unstable higher perchromic acid. The ethereal solution of perchromic acid is gradually decomposed by hydrogen peroxide. Permonophosphoric, pervanadic, and perbenzoic acids are also acted on by hydrogen peroxide.

W. R. S.

**Preparation of Hydrogen Chloride from Chlorine and Water.** H. D. GIBBS (*J. Ind. Eng. Chem.*, 1920, 12, 538—541.)—

By a reversal of the Deacon process, hydrogen chloride may be produced from chlorine and water with the employment of charcoal as a catalyst. The speed of the reaction is governed by the temperature, the relative concentrations of water and chlorine, and the character of the charcoal. For temperatures of 0°, 12°, 25°, and 37·5°, with a charcoal layer of 10 cm. depth and 10·75 sq. cm. cross-section, weight 67 grams, and mesh 8 to 10 per in.; a gas velocity of 500 cm. per min.; air-chlorine ratio, 500:1; water content of air, 50% saturation; pressure of gas above charcoal, 1 atm., and below, 1 atm. less 0·85 cm. water, the curves of production, after the initial rise, gradually flatten. Under the same conditions, but at a temperature of 25°, with water content of 0, 20, 40, and 80% saturation, and ratios of water to chlorine of 0:1, 3:1, 6·2:1, and 12·4:1, the curves indicate that the production of hydrogen chloride in each case reaches a constant rate dependent on the amount of water present. With two varieties of charcoal, a maximum hydrogen chloride production of 34%, falling off to 18% after 800 mins., and of 26%, falling to 7%, was obtained.

W. J. W.

**The Chemical Nature of Sulphur Chloride [Sulphur Dichloride].** MAX BERGMANN and IGNAZ BLOCH (*Ber.*, 1920, 53, [B], 977—979).—The preparation of the trisulphides of benzoic and anisic acids in 70—90% yield by the action of sulphur chloride on the potassium salts of the necessary thio-acid (this vol., i, 548) is of peculiar interest, since the chloride behaves as a definite chemical substance, SCl<sub>2</sub>. The individuality of the compound has, however, been frequently doubted, and it has been regarded as a solution of chlorine or of chlorine and sulphur tetrachloride in sulphur chloride. Were this the case, the action of potassium thiobenzoate on it should yield a mixture of benzoyl di- and tetrasulphides, which might possibly be mistaken analytically for the trisulphide. Examination of molar mixtures of the compounds, however, shows that their physical behaviour is quite unlike that of benzoyl trisulphide, so that there is no possibility of confusion. The experiments therefore confirm the individuality of the chloride, which has previously been shown to be probable by determinations of molecular weight.

H. W.

**Production and Utilisation of Sulphur Dichloride.** (Str.) WILLIAM JACKSON POPE and CHARLES THOMAS HEYCOCK (*Brit. Pat.* 142879).—The employment of 1% by weight of finely

powdered absorbent charcoal as a catalyst greatly facilitates the reaction between chlorine and sulphur monochloride, and similarly, when sulphur dichloride is subjected to conditions which lead to its decomposition into chlorine and the monochloride, recombination is facilitated by similar means.

G. F. M.

**Arsenic-free Sulphuric Acid.** K. SCHERINGA (*Pharm. Weekblad*, 1920, 57, 421—422).—The greater part of the arsenic may be removed by heating the acid, after the addition of a little sulphite, so that some vapour is given off continuously. The acid is then diluted with an equal volume of water and electrolysed for at least one day.

W. S. M.

**Absorption of Nitrogen Oxides by Dilute Nitric Acid.** ERIC K. RIDEAL (*J. Ind. Eng. Chem.*, 1920, 12, 531—538).—The absorption of nitrogen dioxide by dilute nitric acid in presence of air was investigated with 10, 5, and 1%  $\text{NO}_2$ -air mixtures with nitric acid containing 50, 25, 10, and 8%  $\text{HNO}_3$  at temperatures of 30°, 40°, and 50°, and the results are plotted on curves. Absorption in strong nitric acid proceeds most rapidly at low temperatures, but with water the reverse occurs. The point of inversion, that is, where absorption is independent of temperature, is reached with approximately 10% nitric acid. The limitation of the nitric acid concentration to 64% in absorption towers is caused by reduction of nitric acid by the nitrogen trioxide produced. The equilibrium constant of  $2\text{HNO}_3 + \text{N}_2\text{O}_3 = \text{H}_2\text{O} + \text{N}_2\text{O}_4$  at ordinary temperatures is  $K=0.81$ . By agitation with oxygen, the  $\text{N}_2\text{O}_3$  is converted into  $\text{NO}_2$ , and a higher strength of nitric acid is obtained, and by cooling a 12%  $\text{NO}_2$ -air mixture to 20° to remove excess of water above that required for the equation  $2\text{N}_2\text{O}_4 + 2\text{H}_2\text{O} + \text{O}_2 = 3\text{HNO}_3$ , and then refrigerating to -10°, nitric acid of 61.2—78.1%  $\text{HNO}_3$  was produced.

W. J. W.

**Pressure Measurements of Corrosive Gases. The Vapour Pressure of Nitrogen Pentoxide.** FARRINGTON DANIELS and ARTHUR C. BRIGHT (*J. Amer. Chem. Soc.*, 1920, 42, 1131—1141).—An apparatus is described whereby the pressure of corrosive gases may be measured to a fraction of a millimetre. The essential part of the apparatus is a glass diaphragm, 1 cm. diameter and 0.1—0.2 mm. thick, made by flattening the bottom of a small bulb. The flat place and a short length of the stem are thickly coated with platinum, a glass arm with a rounded end, also platinised, is fused to the tube a short distance below the platinum coat, and bent twice at right angles, so that the rounded end just touches the flattened diaphragm, thus making an electrical contact between them. The arm and diaphragm are connected by means of platinum wires with a low-voltage cell and a galvanometer. The diaphragm is mounted in the apparatus containing the corrosive gas, so that the underside comes in contact with the gas, whilst the top is in contact with a variable air

pressure, which can be measured. Changes of pressure deflect the diaphragm and break the circuit, so that it is comparatively simple to see when the pressure of the gas under investigation is exactly balanced by a measured air pressure. This manometer has been used to determine the vapour pressure of nitrogen pentoxide at temperatures 243.0–305.5° abs. Nitrogen pentoxide was prepared by placing 25 c.c. of 100% nitric acid in a glass-stoppered wash-bottle and mixing with small quantities of phosphorus pentoxide until a thick paste was obtained. The mixture was kept in ice and salt during the mixing. The bottle was then connected with a U-tube containing phosphoric oxide, a second empty U-tube immersed in ice and salt to collect the pentoxide, and a protecting U-tube of phosphoric oxide. The mixture was warmed to 35–40°, and the system of tubes subjected to intermittent exhaustion. In this way, 5–10 grams of crude nitrogen pentoxide were condensed in two hours. The nitrogen pentoxide was purified by sublimation in a current of dry ozonised air, and condensed as a colourless, crystalline mass in the experimental tubes. All measurements of vapour pressure were made in the dark, and, since nitrogen pentoxide rapidly decomposes in the gaseous state, an estimation of the rate of decomposition was made at each temperature, and the vapour pressure corrected for this. The vapour pressure of nitrogen pentoxide is represented by the empirical formula  $\log P_{\text{mm}} = 12.44/T + 34.1 \log T - 85.929$ , which is more in keeping with the experimental results than the formula of Russ and Pokorny (*Monatsh.*, 1913, **34**, 1027). The experimentally determined values are closely in agreement with those of Russ and Pokorny. The following values were obtained: 258° abs., 13 mm.; 263° abs., 21 mm.; 268° abs., 32 mm.; 273° abs., 51 mm.; 278° abs., 79 mm.; 283° abs., 118 mm.; 288° abs., 183 mm.; 293° abs., 279 mm.; 298° abs., 420 mm.; 303° abs., 620 mm.; 305.5° abs., 760 mm. The heat of sublimation has been calculated for various temperatures; the following values are obtained for various absolute temperatures: 263°, 12,360 cal.; 268°, 12,640; 273°, 12,760; 278°, 13,110; 283°, 13,360; 288°, 14,160; 293°, 14,140; 298°, 14,010.

J. F. S.

**The Transition from Coal to Coke.** ERIC SINKINEON (*l.* 1920, 117, 839–843).

**The Oxidation of Coals.** MARCEL GODCHOT (*Compt. rend.*, 1920, 171, 32–34).—The coal used was divided into two fractions by extraction with pyridine. The original coal gained 3.15% by weight by oxidation in one month at 100°. The extract and the residue after extraction only gained, under similar conditions, 1.22% and 1.99% respectively, whereas when the coal was reconstructed by mixing extract and residue together, this mixture gained 3.20%. The theory of bacterial action in the oxidation of coal is scarcely in accord with these results, as any such bacteria would have been destroyed during the extraction with pyridine.

W. G.

**The Electromotive Activity of Carbon Monoxide. III.**

K. A. HOFMANN (*Ber.*, 1920, **53**, [B], 914–921. Compare A., 1916, ii, 637; 1919, ii, 23).—The present communication deals with the reactions involved in the oxidation of carbon monoxide at copper surfaces moistened with alkali.

It is found that carbon monoxide is slowly oxidised in open circuit, the electrolyte ultimately containing, in addition to carbonate, traces of formate and scarcely any oxalate; the monoxide is gradually replaced by hydrogen, so that the reaction proceeds according to the scheme:  $\text{CO} + 2\text{KOH} = \text{K}_2\text{CO}_3 + \text{H}_2$ . In the closed circuit, the hydrogen is oxidised to water by oxygen liberated at the opposite electrode. Copper cannot, however, bring gaseous molecular hydrogen into a condition of electromotive activity, but can be very actively charged by nascent hydrogen, most simply by cathodic polarisation.

It appears probable that carbon monoxide, owing to the existence of subsidiary valencies, has the power to unite with alkali hydroxide in the presence of copper to yield small amounts of an isoformate,  $\text{Cu} \dots \text{C}(\text{OH})(\text{OK})$ , which then combines with a further molecule of the hydroxide to yield the alkali carbonate, whilst the hydrogen is liberated in the atomic state at the copper. This conception is supported by the observation that active elements are not formed from copper, carbon monoxide, and water, or from carbon monoxide and alkali hydroxide alone, but only from copper, alkali hydroxide, and carbon monoxide in conjunction. It is further found that hydrated cupric oxide is only reduced by carbon monoxide in the presence of alkali at an appreciable rate if a certain amount of metallic copper is present. Again, the electromotive activity of carbon monoxide at a copper, and to a less degree at a platinum, surface is not immediately developed, whilst, in the absence of hydroxyl ions, carbon monoxide is not noticeably activated by copper. Cuprous oxide does not play a part in the phenomena, since it is found that hydrated cupric oxide is directly reduced in the presence of alkali to the metal, whilst the presence of a minute amount of oxygen diminishes the electromotive force of the system Cu-CO-alkali in a striking, if transitory, manner.

H. W.

**Revision of the Atomic Weight of Silicon. Analysis of Silicon Tetrachloride.**

GREGORY P. BAXTER, PHILIP F. WEATHERILL, and EDWARD O. HOLMES, jun. (*J. Amer. Chem. Soc.*, 1920, **42**, 1194–1197).—The atomic weight of silicon has been determined from the analysis of silicon tetrachloride. The tetrachloride was prepared by the action of chlorine on silicon, filtered to remove ferric chloride, and then kept in contact with mercury for a week in an exhausted flask to remove excess of chlorine. The clear liquid was then carefully fractionated at low temperatures by the method previously described by Baxter and Starkweather for tin tetrachloride (this vol., ii. 436), and sealed into a series of small bulbs. The more volatile portions, which probably contain hydrogen chloride, and the less volatile portions,

which probably contain silicon hexachloride, titanium tetrachloride, and carbon tetrachloride, were rejected. The bulb was weighed and broken under a solution of chloride-free sodium hydroxide, the solution was acidified with nitric acid and precipitated with about the correct amount of pure silver nitrate solution of known concentration, and the end-point determined by means of a nephelometer. As a mean of four experiments, the ratio  $\text{SiCl}_4:4\text{Ag}=0.393815$ , whence the atomic weight of silicon is  $28.111$  ( $\text{Cl}=35.457$ ,  $\text{Ag}=107.880$ ). J. F. S.

**Helium: its Production and Uses. A Lecture Delivered before the Chemical Society on June 17th, 1920.** JOHN CUNNINGHAM MCLENNAN (T., 1920, 117, 923—947).

**Helium in Brannerite.** ROGER C. WELLS (*J. Franklin Inst.*, 1920, 189, 779—780; *Chem. News*, 1920, 121, 22).—The gas liberated when brannerite (this vol., ii, 257) is fused with hydrogen sodium sulphate was found, spectroscopically, to contain helium.

L. J. S.

**Continuous Flow Apparatus for the Purification of Impure Helium Mixtures.** E. EDWARDS and R. T. ELWORTHY (*Trans. Roy. Soc. Canada*, 1919, 13, [iii], 47—52).—Helium containing at least 12% of impurity can readily be purified by passing it in a continuous stream over charcoal at the temperature of liquid air or oxygen. The rate of flow can be increased to at least 10 litres per hour without decreasing the efficiency of the process. The maximum rate of flow was not determined. By the use of two or more sets of charcoal tubes in parallel, the process may be made continuous, as the charcoal may be revived without disturbing the flow. J. R. P.

**Combustibility of Mixtures of Hydrogen and Helium.** JOHN SATTERLY and E. F. BURTON (*Trans. Roy. Soc. Canada*, 1919, 13, [iii], 211—215).—The combustibility was tested by a lighted match and by a white-hot platinum spiral. Under the conditions of experiment, the percentage of hydrogen could be raised to 26 before the mixture became inflammable; if the percentage exceeded 28, the mixture would burn. J. R. P.

**Formation and Decomposition of Sodium Hypochlorite.** F. GIORDANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1919, [iii], 25, 138—153).—Investigation of the action of chlorine on solutions of sodium hydroxide under different conditions shows that the primary action consists in the formation of sodium hypochlorite, and is followed by decomposition of the latter, with formation of chlorate and chloride and liberation of oxygen. The distribution between these two reactions of the active chlorine, which disappears, depends notably on the illumination, the temperature, the concentration of free sodium hydroxide, and the nature of the vessel, and possibly on other factors.

The formation of hypochlorite is accompanied by increase in volume, which must be taken into account in calculating the amount of sodium hydroxide required to yield hypochlorite of definite titre.

The concentration of the free sodium hydroxide in the product exerts a marked influence on the stability. Contrary to Lunge's interpretation ("Sulphuric Acid and Alkali," Vol III, 1911), of Cotellet and Descosses' results (*Mon. Sci.*, 1903, 624), perfectly neutral sodium hypochlorite solution is not stable, but undergoes rapid decomposition. In practice, the action is best arrested when the solution contains 1.5% of sodium hydroxide.

The statement that the law, according to which the percentage decomposition of the hypochlorite per unit time varies with the concentration, is not in agreement with theoretical considerations is erroneous.

T. II. P.

**The Arsenites of Lithium and Potassium.** F. A. H. SCHREINEMAKERS and (Mlle) W. C. DE BAAT (*Rec. trav. chim.*, 1920, 39, 423—428).—A study of the ternary system, lithium oxide-arsenious oxide-water, at 25° shows the existence of one arsenite  $\text{LiAsO}_2$ , which is soluble in water without decomposition. A similar study shows that potassium gives two arsenites,  $\text{K}_2\text{As}_2\text{O}_7$  and  $\text{K}_2\text{As}_2\text{O}_9 \cdot 12\text{H}_2\text{O}$ , both of which are soluble in water without decomposition.

W. G.

**Crystal Structure of Cæsium Dichloro-iodide.** RALPH W. G. WYCKOFF (*J. Amer. Chem. Soc.*, 1920, 42, 1100—1116).—Cæsium dichloro-iodide has been stated to crystallise in two forms, rhombic and hexagonal (rhombohedral). The rhombohedral form is obtained by dissolving 10 grams of cæsium chloride in 50 c.c. of water, adding 8 grams of iodine, and passing chlorine through the hot solution until the iodine has dissolved. On cooling slowly, six-sided plates, about 1 cm. diam. and less than 1 mm. thick, are formed. All attempts to prepare the rhombic variety failed. When the method recommended by Wells and Penfield (A., 1892, 773) was used, crystals were obtained which appeared to be rhombic, but, when examined by the X-rays, the pattern indicated that they were twinned, and on breaking the crystals, they were frequently found to be hollow. The density of the rhombohedral form is found to be 3.86. The structure of the crystals was obtained from the X-ray spectrum obtained from the anticathode of an X-ray bulb, using the crystal as a grating, and from a study of the Laue patterns obtained by passing X-rays through a section of the crystal. It is shown that the body-centred unit rhombohedron contains one molecule. The cæsium atom is placed either at the centre or the corner of this unit, and the iodine atom either at the corner or the centre. Two chlorine atoms lie on the long diagonal very close to 0.31 of its length from the corners. Because of the supposedly very nearly equal scattering power of cæsium and iodine, it is impossible at present to decide between the two possibilities.

J. F. S.

**Additive Compounds of Ammonia with Ammonium Haloids.** JAMES KENDALL and J. G. DAVIDSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1141—1145).—The freezing-point curves of the ammonium haloids with ammonia have been determined over the whole available composition range. It is shown that in the case of ammonium fluoride, no compounds are formed, and that this substance is practically insoluble in liquid ammonia. In the other cases, the following compounds are shown to exist,  $\text{NH}_4\text{Cl}\cdot 3\text{NH}_3$ , m. p.  $10\cdot 7^\circ$ ;  $\text{NH}_4\text{Br}\cdot 3\text{NH}_3$ , m. p.  $13\cdot 7^\circ$ ;  $\text{NH}_4\text{I}\cdot 3\text{NH}_3$ , m. p.  $-8\cdot 0^\circ$ ; and  $\text{NH}_4\text{I}\cdot 4\text{NH}_3$ , m. p.  $-5\cdot 1^\circ$ . Other compounds of these systems previously recorded were not observed, and in all probability do not exist. The stability of the additive compounds with ammonia increases regularly as the series of the ammonium haloids is ascended, and it is therefore held to be likely that some of these compounds may be capable of existence in the vapour phase.

J. F. S.

**Some Reactions started by a Primer.** ERNEST BERGER (*Compt. rend.*, 1920, **170**, 1492—1494).—Numerous reactions, when started by localised heating, will spread throughout the whole mass. The priming mixture suggested by the author consists of sixty parts of potassium nitrate or sodium nitrate and forty parts of industrial calcium silicide. This mixture can be lit with a match, and its combustion produces a very high temperature. It has been used to start such reactions as the reduction of boron phosphate or arsenate by aluminium, the reduction of calcium or barium sulphate by red phosphorus, the preparation of silicon and boron fluorides from lead fluoride.

W. G.

**Production of Chlorides by Primed Reactions.** ERNEST BERGER (*Compt. rend.*, 1920, **171**, 29—32. Compare preceding abstract).—Aluminium will replace a number of metals and metalloids from their chlorides by spontaneous action or by a primed reaction. In some cases, magnesium is still more active. In the same way, a considerable number of metals, such as calcium, magnesium, aluminium, manganese, etc., will displace the carbon from organic chlorides, such as carbon tetrachloride, tetra- and hexa-chloroethane, and chloroform. Such actions, when started, continue with the generation of a considerable amount of heat, the metallic chloride being vaporised. In the case of liquid organic chlorides, these may first be absorbed in kieselguhr or sawdust. Such mixtures found application in the production of smoke clouds during the war.

W. G.

**Complex Salt Formation.** E. H. RIESENFELD and H. FELD (*Zeitsch. Elektrochem.*, 1920, **26**, 286—288).—A solution of barium sulphate in 90% sulphuric acid has been electrolysed between platinum electrodes by a current of 190 milliamperes and 440 volts. After the current had passed for seven and a-half hours, the change in concentration in the anode and cathode cells was determined.

The results show that the barium migrates to the anode as a complex ion, and that in consequence the compound usually termed barium hydrogen sulphate must be regarded as a complex acid of the formula  $H_2[Ba(SO_4)_2]$ . Similar experiments were carried out with a solution of silver chloride in 35% hydrochloric acid, and it was found that here also a complex acid of the formula  $H[AgCl_2]$  is present.

J. F. S.

**Experimental Determination of the Vapour Pressure Curves of Molten Cadmium and Zinc, and the Calculation of the Chemical Constants of Cadmium, Zinc and Monatomic Bromine.**

H. BRAUNE (*Zeitsch. anorg. Chem.*, 1920, 111, 109—147).—The vapour pressure of molten cadmium and zinc has been determined for small pressures (up to 79 mm.) by the circulation method, and for pressures up to 2 atms. by the boiling-point method. The results are represented by the equations,  $\log p = -5763/T - 1.28 \log T + 12.282$  for cadmium, and  $\log p = -6655/T - 1.147 \log T + 12.046$  for zinc. The specific heats of the molten metals have been determined over a considerable range of temperature. The atomic heats calculated from the specific heats are practically constant over the temperature range between the melting point and the boiling point. The values found are: cadmium 7.50, zinc 7.24. The chemical constant of both elements was calculated from the vapour-pressure measurements, and the values  $1.54 \pm 0.2$  for cadmium and  $1.11 \pm 0.7$  for zinc obtained, which are in keeping with theory for the chemical constants of monatomic gases. The chemical constant of monatomic bromine has been determined from Bodenstein's measurements of the dissociation of bromine (A., 1916, ii, 552). The calculation could not be strictly carried out because of lack of information on the specific heat of bromine at low temperatures; nevertheless, the values obtained are shown not to be at variance with the theory of the chemical constants of monatomic gases.

J. F. S.

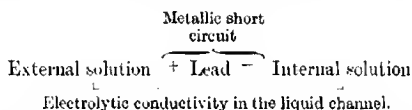
**The Transmutation of Simple Substances.** LAURENT NAUDIN (*Mon. Sci.*, 1920, [v], 10, 121—122).—A very brief account of unpublished experiments of Schützenberger, in which he found that, when lead, carefully purified from silver, was chlorinated by chlorine gas and subsequently reduced by hydrogen at a high temperature, the lead then contained traces of silver. This process was repeated several times on the same sample of lead, carefully purified between each process, always with the same results.

W. G.

**Formation of the Autogenous Lead-tree.** A. THIEL (*Ber.*, 1920, 53, [B], 1066—1072).—It has been shown by Senderens that a lead-tree is formed when the metal is immersed in solutions of certain lead salts, and the phenomenon has been explained by Cohen and Helderman (A., 1915, ii, 456) on the basis of the presumed allotropic forms of lead. Since the author has shown, how-



ever, that lead does not form allotropes (following abstract), this explanation is no longer tenable. Crystallographical examination of autogenous and other lead-trees, of electrolytic lead, and of solidified lead shows the crystals to be invariably of the same type and to be composed of combinations of octahedron and cube. The formation of the autogenous tree occurs uniformly under acidified solutions of lead nitrate, but very seldom (in two cases out of fifty) under Heller's solution. The explanation is to be found in the author's theory of desglomeration (following abstract). Local ionic concentration systems are set up in the interstices between the crystallites as the nitrate solution penetrates into them, and becomes exhausted without the possibility of free admixture with the external, less exhausted solution. There are thus formed short-circuited ionic concentration cells, thus:



in consequence of which the lead-tree becomes developed at irregular positions over the whole surface of the metal. With Heller's solution, the tendency towards the formation of such cells is much less pronounced, since under the most favourable conditions the potential developed does not exceed 10 millivolts, whilst with the nitrate solutions it may even exceed 40 millivolts. H. W.

**The supposed Allotropy of Lead.** A. THIEL (*Ber.*, 1920, 53, [B], 1052-1066).—It has been shown by Heller (A., 1915, ii, 634) that compact lead ultimately crumbles to a powder when preserved beneath acidified solutions of lead salts, and the phenomenon has been attributed to allotropic change. The results, and also the nature of the product, have been confirmed by Cohen and Heldermann (A., 1915, ii, 456), who, however, consider that several allotropes are formed. The author's experiments, on the other hand, lead him to the conclusion that the phenomenon is not due to allotropy, but to simple chemical action.

The majority of the experiments were performed with samples of commercial soft lead containing about 0.005% of iron, and no other impurity in detectable amount. In consequence of the difficulties regarding the supply of gas, they were generally effected at the ordinary temperature, about 18°, although at times the temperature fell as low as 0°. In conformity with Heller's solution (molar with respect to lead acetate and 0.4N with respect to nitric acid), the solutions were, in general, molar as regards lead salt and 0.4N as regards acid. Strips of lead weighing 8-10 grams, which had previously been repeatedly etched by dilute nitric acid, were immersed in about 10 c.c. of the necessary solutions.

The disintegration of lead is only observed in solutions which

contain nitrate ions, and does not occur, for example, with lead acetate and acetic acid, lead chloride and hydrochloric acid, lead nitrite, lead silicofluoride and hydrofluosilicic acid, lead perchlorate and perchloric acid. Disintegration which has been started in specimens of lead by Heller's solution is arrested when they are transferred to nitrate-free solutions. Lead is slowly attacked when immersed in Heller's solution, nitrogen and nitric oxide being evolved, and the metal being considerably dissolved previous to the commencement of the stage at which it begins to fall to powder. Similarly, the metal is attacked by solution of nitrates which are free from lead; reaction, however, starts more slowly, so that it would appear that the process is catalysed by the presence of lead ions or lead nitrite.

Further evidence against the theory of the formation of an allotrope of lead is afforded by inspection of the disintegrated product, which is found to consist of homogeneous, irregularly polyhedral granules with more or less rounded edges; these are, in general, relatively large in size and free from small crystals, such as would be expected if a new modification had been formed. Again, according to Cohen and Heldermaun, the transition temperature lies at about  $50^{\circ}$  ( $60^{\circ}$  according to Jänecke), above which the compact modification is stable; it is found, however, that lead rapidly disintegrates under Heller's or other solution containing nitrate at  $100^{\circ}$ , although unaffected under these conditions in acidified lead acetate and lead perchlorate solutions. Lastly, only a very slight difference of potential is observed between compact and disintegrated lead immersed in lead perchlorate solution.

The author explains the phenomenon in the following manner. Compact lead is composed of crystallites, the crevices of which are filled by a finely granular eutectic, which is present even in "pure" metals (a similar structure must be assumed for all metals which have solidified from the molten state). This eutectic is more readily attacked by a suitable agent when the impurities are more chemically active than the metal itself; in consequence, cavities are formed around the crystallites, which finally become so deep that the latter are completely detached from the main mass. (The term "disglomeration" is proposed for the phenomenon.) In support of this hypothesis, it is shown that disintegration can also be effected by other suitable agents, as, for example, when a lead anode slowly dissolves in a solution of perchloric acid, although the action is less marked in this case. On the other hand, disglomeration is only to be expected when dealing with solidified metals, and it is interesting to note that lead crystals, in the form of the lead-tree, are only resolved into the individual crystals when immersed in hot or cold Heller's solution, whilst, further, massive lead can be protected from disintegration by coating it with a deposit of electrolytic lead. Attempts are also described to find other instances of disglomeration, and it is shown that copper can be disintegrated by immersion in ammoniacal persulphate solution.

H. W.

**The Composition of Ancient Eastern Bronzes.** MASUMI CHIKASHIGE (T., 1920, 117, 917—922).

**Colloidal Cuprous Oxide.** C. PAAL (*Zeitsch. anal. Chem.*, 1920, 59, 166—167).—Referring to a method described by RUOSS (A., 1919, ii, 367) for the preparation of colloidal cuprous oxide, the author points out that the substance has been known for some considerable time (compare A., 1906, ii, 356, 358; 1914, ii, 656).

W. P. S.

**The Precipitation of Mercuric Salts by Hydrogen Sulphide.** PIERRE JOLIBOIS and PIERRE BOUVIER (*Compt. rend.*, 1920, 170, 1497—1498).—Using the apparatus previously described (this vol., ii, 107, 112) to study the action of varying proportions of hydrogen sulphide on mercuric chloride in dilute solution, it is shown that the black precipitate, formed with excess of hydrogen sulphide, has the composition  $\text{HgS}$ , and the white precipitate, formed in the presence of excess of mercuric chloride, has the composition  $2\text{HgS}, \text{HgCl}_2$ . There is no indication of the existence of any other intermediate compound.

W. G.

**Corrosion of Iron.** R. KATTWINKEL (*Zeitsch. angew. Chem.*, 1920, 33, i, 156).—An incrustation which formed in a steam pipe had strong magnetic properties, and consisted almost entirely (99.12%) of magnetic iron oxide,  $\text{Fe}_3\text{O}_4$ .

W. P. S.

**Action of Metallurgical Additions on the Anomaly of the Dilatability of Nickel Steels.** CH. ED. GUILLAUME (*Compt. rend.*, 1920, 170, 1433—1435).—A detailed study of the action of manganese, chromium, and carbon on the dilatability of nickel steels over the range of easily obtainable alloys, and of a series of nickel steels containing 5% of copper. The addition of any of these third constituents diminishes the intensity of the anomaly of dilatability in the region of its minimum value. In the case of manganese, carbon, and copper, within a limited region of nickel content, ternary alloys are obtained which are slightly less dilatable than the binary alloys with the same nickel content.

If the other constituents are well known, the measurement of the dilatability gives a method of fixing the carbon content to within 1 in 10,000.

W. G.

**Values of the Dilatabilities of Nickel Steels.** CH. ED. GUILLAUME (*Compt. rend.*, 1920, 170, 1554—1557. Compare preceding abstract).—Using nickel steels containing 0.4% of manganese and 0.1% of carbon, the true dilatabilities first decrease to a minimum as the nickel content increases, and then increase again. The minimum value of the dilatability,  $\alpha_{20} 1.19 \times 10^{-6}$ , corresponds with a nickel content of 35.6%. Allowing for the coefficients of dilatability of manganese and carbon, it is shown that such an alloy of pure iron and nickel would have a dilatability equal to  $0.2 \times 10^{-6}$ .

W. G.

**Thermal Change of the Elastic Properties of Nickel Steels.** P. CHEVENARD (*Compt. rend.*, 1920, 170, 1499—1502).—A study of the anomaly of elasticity of twenty-eight nickel steels containing varying proportions of nickel and only just the amount of manganese indispensable to forging. The method employed was to measure the time and decrement of oscillation of a torsion pendulum constructed with wires of the steels.

The coefficient of variation of the modulus of torsion is characterised, in reversible alloys, by a rapid increase to a maximum, which corresponds with the minimum of dilatability, and then a gradual diminution. For alloys with a stable state in the cold, the results do not indicate any irregularity.

Tempering and hammer hardening diminish the value of the modulus of torsion, which increases, however, with the temperature of annealing, there being a maximum of rapidity between 450° and 550°.

As in the case of the dilatability, the thermo-elastic coefficient is affected by the treatment which the alloy undergoes. Contrary to what happens in the case of the dilatability, however, hammer hardening diminishes the amplitude of the anomaly, whilst tempering increases it.

W. G.

**The Constitution of the Lilac-grey Complex Chromium Sulphate.** A. RECOURA (*Compt. rend.*, 1920, 170, 1494—1497).—The lilac-grey chromium sulphate previously described (this vol., ii, 114) consists of one molecule of the green chromium sulphate and two molecules of the normal violet sulphate. When freshly prepared, the  $\text{SO}_4^{''}$  ions corresponding with the green sulphate are masked, whilst the  $\text{SO}_4^{''}$  ions corresponding with the violet salt are precipitable. On keeping, the latter  $\text{SO}_4^{''}$  ions also become masked. The explanation given is that in the freshly-precipitated lilac-grey salt the green sulphate is in its depolymerised state, but, once solid, it rapidly and spontaneously becomes converted into its polymerised form, and in this form is capable of masking the  $\text{SO}_4^{''}$  ions of the violet salt.

W. G.

**Bromination of Antimony in Ethereal Medium.** A. RAYNAUD (*Bull. Soc. chim.*, 1920, [iv], 27, 411—414).—When an excess of dry bromine is added to finely powdered antimony in dry ethyl ether and the liquid boiled for three hours, a crystalline compound, having the composition  $\text{SbBr}_3 \cdot \text{OEt}_2$ , is obtained. When freshly prepared, it does not fume in air, but is decomposed by water. The ether is only removed by heating the compound at 55°. When exposed on a porous plate in a bell-jar over sulphuric acid, the compound is, in a few days, converted into antimony tribromide.

W. G.

## Mineralogical Chemistry.

**Graphite in Japan.** SELJIRŌ NODAN<sup>a</sup> (*Beitr. Min. Japan*, 1915, No. 5, 260—261).—The various modes of occurrence and origin are briefly discussed. The following analyses show that the scaly graphite from crystalline rocks contains more carbon and less volatile matter than the compact graphite from metamorphosed sedimentary rocks (of Palaeozoic and Mesozoic age):

Rock Matrix.	C.	S.	Volatile matter, %	H <sub>2</sub> O.	Ash.
Gneiss .....	88.87	trace	1.86	0.53	8.74
Granite .....	58.00	trace	2.22	0.40	39.38
Palaeozoic .....	20.85	0.44	7.40	0.49	71.24
Mesozoic .....	1.36	0.03	6.72	0.42	91.50

L. J. S.

**Tetrahedrite from Besshi Mines, Prov. Aichi, Japan.** KOTOJIRŌ ARAI (*Beitr. Min. Japan*, 1915, No. 5, 267—268).—Analysis by K. ISHII gave:

Cu.	Sb.	As.	Bi.	S.	Fe.	Ag.
33.672	30.538	0.227	0.139	26.789	4.424	0.41067
Au.	Mn.	Ni.	Co.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.
0.0005	0.007	0.007	trace	1.052	1.48	0.30

Mercury, zinc, lead, and tin are absent.

L. J. S.

**Calcite Deposit from the Senami Hot Spring, Japan.** DENZŌ SATŌ (*Beitr. Min. Japan*, 1915, No. 5, 281—282).—From a boring made in prospecting for oil at this locality, water at a temperature of 100° gushed out to a height of 20 metres, and the oil concession became a spa. A snow-white, crystalline crust is deposited by the water, and the pipe and conduit have frequently to be cleared. The water is clear and colourless, neutral in reaction, and slightly alkaline in taste, D<sub>14</sub> 1.0035. Analysis gave, in grams per litre:

K.	Na.	Ca.	Mg.	Cl.
0.0786	1.3333	0.1323	0.0003	2.1162
SO <sub>4</sub>	H <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> SiO <sub>3</sub> .	CO <sub>2</sub> .	Total.
0.2759	0.0632	0.1928	0.1596	4.3522

Analysis I is of the lower layer, with a slight grey tinge, and II of the colourless, transparent upper layer. D<sub>20</sub> 2.72. Rhombohedra of calcite, with curved faces, are present in the drusy portions:

	CaO.	MgO.	MnO.	Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .	CO <sub>2</sub> .	H <sub>2</sub> O.	Total.
I ...	55.14	trace	0.35	0.50	0.36	43.25	0.32	99.92
II .	55.57	—	0.29	0.27	0.14	43.65	0.30	100.22

L. J. S.

**Aragonite Cones formed at the Kuriyama Geysers, Prov. Shimotsuke, Japan.** WATARU WATANABE (*Beitr. Min. Japan*, 1915, No. 5, 237—241).—Hot (94°) water, with a sulphurous odour, issuing from rock crevices gave, on analysis by M. KAWAKITA (grams per litre):

NaCl.	HNaCO <sub>3</sub> .	CaCO <sub>3</sub> .	Na <sub>2</sub> SO <sub>4</sub> .	K <sub>2</sub> SO <sub>4</sub> .	MgCO <sub>3</sub> .	MnCO <sub>3</sub> .	FeCO <sub>3</sub> .
1.1642	0.1241	0.1600	0.1134	0.0531			traces

DE 1.02. The water has an alkaline reaction after boiling. The material of the aragonite cones deposited by this water gave, on analysis by Y. OSHIMA:

CaCO <sub>3</sub> .	SrCO <sub>3</sub> .	BaCO <sub>3</sub> .	MnCO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> .	Insol.*	Total.
93.26	0.65	0.50	0.99	1.32	3.12	99.84

\* Consisting chiefly of free sulphur and some organic matter.

The interior of the cones consists of calcite, and the central channel through which the water passes is lined with pink crystals of mangano-calcite. A cone, measuring 30 cm. across the base, 30 cm. high, and weighing 13.878 kilos., was formed around an orifice during a period of ten months; and when it was broken off, another cone grew in its place. Some extinct geyser cones at another district in Japan reach a height of 4 metres; these are now transformed into calcite. The hot springs deposit volatile sulphides, such as orpiment, realgar, and cinnabar. L. J. S.

**Calcareous Deposit from Hot Spring Water at Hokuto, Formosa.** KOTORA JINBO (*Beitr. Min. Japan*, 1915, No. 5, 183).—In reservoirs of the hot water, calcium carbonate is deposited as minute, irregular, disk-shaped aggregates of very fine acicular crystals. The deposit is brown in colour, and gave, on analysis by SÆGER:

CaO.	SrO.	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CO <sub>2</sub> .	Ign.
38.74	trace	0.39	6.29	0.86	43.63	3.81

L. J. S.

**Refractive Indices of the Rhombohedral Carbonates.** FAUBERT (*Bull. soc. franc. min.*, 1919, 42, 88—120).—The measured values of the refractive indices of isomorphous mixtures of these carbonates agree closely with those calculated from their chemical composition by the formulae of Mallard. The following method for distinguishing magnesite from the other carbonates is given: The powdered sample is heated to a red heat and a drop of cobalt nitrate solution is added, after cooling. A bluish-green coloration immediately develops around particles of all carbonates except magnesite.

CHEMICAL ABSTRACTS.

**Pyramite (Ferberite and Hübnerite) from Japan.** KOTORA JINBO (*Beitr. Min. Japan*, 1915, No. 5, 256—259).—It occurs with rock-crystal in quartz veins at Kurasawa,

Kai. It is sometimes replaced by brownish-black ferberite (anal. I), these pseudomorphs having been originally described as tetragonal iron tungstate under the name "reinite." Microscopic crystals of hair-brown to dark red hübnerite (anal. II) occur with scheelite in gold-quartz at Nishizawa.

	WO <sub>3</sub>	FeO.	MnO.	CaO.	MgO.	Total.
I .....	75.214	24.372	0.185	—	—	99.771
II .....	74.25	3.18	20.84	1.01	trace	99.28

L. J. S.

**Thaumasite and Spurrite from California.** W. F. FOSHAG (*Amer. Min.*, 1920, 5, 80—81).—Small needles of thaumasite form interlaced masses and fibrous veins in a rock composed of akermanite and spurrite (A., 1909, ii, 61) in the crystalline limestones at Crestmore, California (A., 1919, ii, 113). Analysis gave:

SiO <sub>2</sub> .	(Al,Fe) <sub>2</sub> O <sub>3</sub> .	CaO.	SO <sub>3</sub> .	H <sub>2</sub> O+CO <sub>2</sub> (ign.).	Total.
9.10	0.84	12.98	27.56	49.48	99.96

The spurrite shows polysynthetic twinning, and is optically negative with  $\alpha$  1.638,  $\beta$  1.676. Since the rock contains 4.64% CO<sub>2</sub>, it follows that spurrite forms half the mass. Thaumasite has evidently been derived from spurrite by the action of sulphated waters, although sulphates are rare in the deposit. L. J. S.

**Mineralogy of Korea (Chosen).** NOBUYO FUKUCHI (*Beitr. Min. Japan*, 1915, No. 5, 207—227).—Sixty mineral species are described. Yellow to brown crystals of orthoclase with a violet-blue schiller (moonstone) from Sözen gave K<sub>2</sub>O 6.43, Na<sub>2</sub>O 6.53%, D 2.60. Crystals of zircon from Jidö gave SiO<sub>2</sub> 33.06, ZrO<sub>2</sub> 63.32, Fe<sub>2</sub>O<sub>3</sub> 3.33, TiO<sub>2</sub> nil; total, 99.71. The material is colourless, but it shows a dark violet on the surface and along cracks. Several partial analyses are given of phlogopite, ranging from MgO 23.77, FeO 1.47% in the colourless variety to MgO 4.52, FeO 3.45% in the black. L. J. S.

**Crystalline Nodules in Agalmatolite from Mitsuishi, Japan.** HIDEYUKI AWAZU (*Beitr. Min. Japan*, 1915, No. 5, 298—299).—The minute crystals composing the nodules are colourless with a perfect cleavage, and are doubtfully referred to gibbsite. [The following analysis suggests, however, that the material consists of diaspore with intermixed opal, as described by Y. Chitani (*J. Geol. Soc. Tokyo*, 1915, 22, 384; see *Mineralogical Abstracts*, 1920, 1, 64).]

Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	CO <sub>2</sub> .	SiO <sub>2</sub> .	H <sub>2</sub> O.	Total.
70.43	0.32	0.01	0.03	0.35	14.37	14.38	99.89

L. J. S.

**Analcite from Maze, Japan.** SEIGO SUMIZU (*Beitr. Min. Japan*, 1915, No. 5, 295).—The following analysis agrees with the formula Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, 4SiO<sub>2</sub>, 2H<sub>2</sub>O:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
54.58	23.05	nil	0.10	0.45	nil	13.50	8.70	100.38

L. J. S.

**Axinite Crystals from Japan.** MASAOKI HOSHINA (*Beitr. Min. Japan*, 1915, No. 5, 294—295).—Pale violet-grey axinite, forming with quartz the gangue of copper ores at Ōgiyama, gave:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO	MgO	Ign.
45.20	15.61	6.84	6.33	22.80	0.82	0.32

L. J. S.

**Chlorite from Jōdoyama, Japan.** DENZŌ SATŌ (*Beitr. Min. Japan*, 1915, No. 5, 296—298).—Loose blocks occurring on the surface of the granite-gneiss mountain of Jōdoyama consist of an aggregate of garnet, quartz, calcite, and dark green chlorite. The last of these gave on analysis:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO	MgO	Ign.	Total	Sp. gr.
30.12	11.80	35.22	3.29	5.81	3.58	10.27	100.09	3.25

L. J. S.

**Epidote Crystals from Katakai, Japan.** KINZŌ NAKASHIMA (*Beitr. Min. Japan*, 1915, No. 5, 253—255).—Large, brownish-green to greyish-green crystals embedded in massive, milky quartz gave:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO	MgO	H <sub>2</sub> O	Total
38.34	27.45	8.81	0.86	0.21	23.21	0.31	2.21	101.40

L. J. S.

**Diabantite, Stilpnomelane, and Chalcodite from Westfield, Massachusetts.** EARL V. SHANNON (*Proc. U.S. Nat. Mus.*, 1920, 57, 397—403).—The diabase exposed in the trap quarries of this district is more or less altered with the formation of dark green, earthy, chloritic decomposition products. These are usually not sufficiently pure for chemical investigation, but better material was obtained from certain fissures. I is the mean of four analyses of diabantite. This is dark green and clayey when wet, but on drying it shrinks and cracks to a friable, pale olive-green mass. D 2.77. The minute micaceous scales are optically negative and sensibly uniaxial. Heated in the closed tube, it becomes brown, yields neutral water, and finally fuses to a black, magnetic glass. It is readily soluble in hot hydrochloric or sulphuric acid, and fuses easily in nitric acid, in each case with the separation of flocculent silica. II is the mean of two analyses of stilpnomelane obtained from another fissure, but with the same general appearance as the diabantite; it is, however, more blue, more plastic, has a peculiar sub-metallic lustre, and the dried material is compact and tough. The two minerals can be distinguished by their behaviour in boiling nitric acid (D 1.20). Diabantite dissolves slowly without change, whilst stilpnomelane is wholly oxidised, forming a rust-like, brown material. Analysis III is of chalcodite, which is found only in small amount as a scaly coating with a golden-yellow colour and metallic lustre. A minute amount



of pure material contained  $\text{SiO}_2$  45.77%, with much ferric iron, no ferrous iron, and very little alumina and magnesia. This is evidently an indefinite oxidation product of stilpnomelane; in some cases it still showed a green core containing ferrous iron.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{MnO}$	$\text{CaO}$	$\text{MgO}$	$\text{H}_2\text{O}$ (at 105°)	$\text{H}_2\text{O}$ (>105°)	Total
I.	28.15	15.17	3.85	25.23	0.21	0.59	14.56	0.57	11.25	99.58
II.	44.08	4.74	5.27	23.31	0.87	trace	8.36	2.21	10.28	99.12
III.	44.61	6.75	23.59	—	—	—	—	6.21	7.14	98.19

L. J. S.

**The Cumberland Falls (Whitley Co., Kentucky) Meteorite.**  
 GEORGE P. MERRILL, with analyses by EARL V. SHANNON (*Proc. U.S. Nat. Mus.*, 1920, **57**, 97—105).—This stone, which fell on April 9th, 1919 (this vol., ii, 47), represents a new type of meteorite, for which the name *Whitleyite* is suggested. It is a coarse breccia consisting of a chalky-white to grey portion in larger amount, with enclosed angular blocks of a black chondritic stone. The two portions each represent different types of stones, and the whole mass shows much evidence of crushing and distortion. The lighter-coloured portion (bulk analysis I) consists mainly of enstatite intimately intergrown with a monoclinic pyroxene, and with small quantities of diallage, nickel-iron, troilite, and graphite. The dark portion (bulk analysis II) owes its colour to finely-disseminated graphite and metallic particles:

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$	$\text{P}_2\text{O}_5$	$\text{FeO}$	$\text{NiO}$
I.....	55.172	0.382	0.062	trace	2.916	0.123
II.....	41.633	1.537	0.591	trace	9.399	0.211
	$\text{CoO}$	$\text{CaO}$	$\text{MgO}$	$\text{MnO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$
I.....	trace	1.586	38.734	0.112	0.157	0.150
II.....	trace	4.059	27.848	—	trace	trace
	$\text{Fe}$	$\text{Ni}$	$\text{Co}$	$\text{Cu}$	$\text{Mn}$	$\text{Cr}$
I.....	0.888	0.059	0.004	0.003	0.005	trace
II.....	12.108	0.747	0.073	0.001	0.088	trace
	$\text{S}$	$\text{P}$	$\text{Cl}$	$\text{C}$	$\text{H}_2\text{O}$	Total (less C for Cl, S, P)
I.....	0.784	0.034	0.028	0.164	0.167	100.961
II.....	2.464	0.014	0.045	0.449	0.210	100.084

The percentage composition of the metallic portion of each is given under Ia and IIa respectively:

	$\text{Fe}$	$\text{Ni}$	$\text{Co}$	$\text{Mn}$	$\text{Cu}$	$\text{Cr}$	Total
Ia.....	92.596	6.152	0.417	0.522	0.313	trace	100.000
IIa.....	92.982	5.735	0.599	0.676	0.008	trace	100.000

Ib is of the friable, chalky-white enstatite (with intergrown monoclinic pyroxene), forming the main mass of the lighter portion. IIb of the silicate (22.582%), decomposed by dilute hydro-

chloric acid; and IIc of the insoluble silicate (56.58%) in the darker portion:

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	NiO	CoO	MnO	CaO	MgO	Ign.	Total
I...	59.53	1.09	0.98	nil.	—	—	0.96	37.17	0.33	100.06
II...	38.239	trace	6.566	0.043	trace	0.709	5.246	49.197	—	100.000
II...	58.341	2.705	3.528	0.295	trace	0.562	5.073	29.496	—	100.000

From these analyses, the mineralogical composition of the dark enclosures is: metal, 13.022; troilite, 6.760; lawrencite, 0.080; chromite, 0.869; soluble silicates, mainly olivine, 22.582; insoluble silicates, mainly pyroxenes, 56.580; carbon, mainly amorphous, 0.449; calcium phosphate, trace; hygroscopic water, 0.210; total, 100.552.

L. J. S.

### Analytical Chemistry.

**Filter with Perforated Plate and Wire Gauze.** F. MACH and P. LEDERLE (*Chem. Zeit.*, 1919, **43**, 831).—Silver gauze may be used in place of platinum in the filter described previously by the authors (*A.*, 1919, ii, 303).

W. P. S.

**Iron Basins and their Use in Analysis.** H. SERTZ (*Zeitsch. angew. Chem.*, 1920, **33**, i, 156).—Iron basins are useful for sulphide fusions, particularly when they have been treated previously with nitric acid.

W. P. S.

**The Alteration of Glass Flasks used in Laboratories.** R. DUBRISAY (*Bull. Soc. chim.*, 1920, [iv], **27**, 409—411).—The physico-chemical volumetric method previously described (compare *A.*, 1913, ii, 388) for the estimation of traces of alkali can be used for the estimation of the amount of alkali dissolved from glass vessels when water is boiled in them. The method has been applied to compare the resistance of some French flasks made during the war with that of some pre-war German flasks. The French flasks showed up very well, both in their resistance to attack by boiling water and by boiling alkali.

W. G.

**Methyl-orange as Indicator.** V. MACRÌ (*Boll. Chim. farm.*, 1920, **59**, 193—196).—The author describes the behaviour of methyl-orange in presence of various compounds which affect its action as an indicator (compare *J. Soc. Chem. Ind.*, 1920, August).

T. H. P.

**Use of Conductivity Titrations in Neutralisation Analysis.** III. Titration of Combined Weak Acids or Bases in Salt (Displacement Curves). I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **111**, 97—108. Compare *A.*, 1919, ii, 74, 76).—The quantity of a weak acid or base combined as a salt may

be estimated by titration with a strong base or acid, respectively, using the electrical conductivity as indicator. On adding a strong acid, say, hydrochloric acid, to the salt of a weak acid, the weak acid will be displaced, and, having a low degree of ionisation, the conductivity of the solution will change very little, but as soon as all the weak acid has been liberated, the first drop of strong acid in excess will cause a great increase in the conductivity. On plotting the conductivity against the number of c.c. of standard acid, a sharp break will be found, which represents the point of equivalence. The method is found to work well in all cases where, after displacement of 50% of the weak acid, the conductivity has not increased more than 1%. Examples are given of the titration of sodium acetate, sodium formate, and for weak bases, ammonium chloride. In the case of the dibasic acids in sodium oxalate, sodium tartrate, and sodium citrate, it is found that good results may be obtained here also, if in the last named two cases an equal volume of alcohol is added to the solution before titration.

J. F. S.

**Spectrophotometric Study of the "Salt Effects" of Phosphates on the Colour of Phenolsulphonthalein Salts and some Biological Applications.** CHARLES L. BRIGHTMAN, M. R. MEACHEM, and S. F. ACREE (*J. Bact.*, 1920, **5**, 169-180, Compare A., 1919, ii, 75).—Phosphate solutions, varying in concentration from 0.5*N* downwards and showing the same hydrogen-ion concentration by the hydrogen electrode method, have a marked influence on the colour of phenolsulphonthalein salts. This salt effect becomes small when the phosphate concentration is 0.05*N* or less. The apparent ionisation constant of the phenolic group of the phenolsulphonthaleins varies with the concentration of the phosphate present, and averages about  $2.65 \times 10^{-8}$  when uncorrected for salt effect. When a graphic method is used for calculating the ionisation constant freed from the salt effect of phosphate, the value is lowered to about  $1.95 \times 10^{-8}$ .

CHEMICAL ABSTRACTS.

**Improved Form of McLeod Gauge.** AUSTIN BAILEY (*Chem. News*, 1920, **120**, 302).—A modification of the McLeod gauge, which consists mainly of a three-way tap which connects the mercury reservoir with either an aspirator or the air through a fine jet, and of a movable and interchangeable pressure chamber which permits of the gauge being used over large ranges of pressure. With this apparatus, the danger of the mercury rising too rapidly into the pressure chamber is avoided, because the air can only enter through the fine jet.

J. F. S.

**A Weight Burette for Gas Analysis.** E. R. WEAVER and P. G. LEDIG (*J. Amer. Chem. Soc.*, 1920, **42**, 1177-1185).—A weight burette is described for use in gas analysis. By means of

this, the volume of the sample and changes in volume after absorption of constituents are determined by weighing the quantity of mercury, after compensation, which is expelled from, or taken into, the burette. It is claimed that, with this device, the volumes obtained are very accurate, and the accuracy of the measurement is independent of the state of the meniscus. The readings are quite free from parallax errors, since no graduated scales have to be read. The gas to be measured never comes in contact with a stopcock, rubber tube, or other possible origin of a leak. The apparatus may be made of any desired size. A number of measurements are recorded, and it is shown that the average deviation from the mean value in a single gas estimation is 0.0044%, whilst the maximum divergence is only 0.014%.

J. F. S.

**Theory of the Katharometer.** H. A. DAYNES and G. A. SHAKESPEAR (*Proc. Roy. Soc., A*, 1920, **97**, 273—286).—The katharometer is an instrument designed for automatic registration of small quantities of hydrogen (1%—2%) in air; it is also of considerable use in determining the permeability of balloon fabric to hydrogen. In the present paper, an account is given of the instrument, and this is followed by a theoretical treatment of the principles involved in the use of the instrument. The instrument consists of two small helices of thin platinum wire (ca. 0.001 inch diam.) enclosed each in one of two cells in a copper block; each helix is mounted in a small frame consisting of a loop of copper wire soldered to a ring of copper. This ring is fitted with an insulating plug, through which the copper lead wire is introduced. One extremity of the helix is soldered to the lead and the other to the distal end of the loop. The outer part of the lead passes through a plug of rubber fitting into the cell, and over this rubber an ebonite plug is pressed down by a screw collar. Thus the cell is rendered gas-tight. Both cells are similarly fitted, except that, whilst one is hermetically sealed, the other communicates with the atmosphere by three small holes. The helices constitute two arms of a Wheatstone bridge, and have a resistance of about 8 ohms. The main working current of the bridge is 0.100 ampere, and this gives the wires a temperature about 15° above that of the copper block. Contact with hydrogen, owing to surface combustion, raises the temperature of one helix, and from the change in resistance the amount of hydrogen in the air may be estimated.

J. F. S.

**Titration of certain Chlorides with Silver Nitrate, using Potassium Chromate as Indicator.** H. W. BOLAM (*Chem. News*, 1920, **120**, 292).—When barium, or other metal yielding a chromate less soluble than silver chromate, is present, slightly more chromate than is sufficient to precipitate the barium should be added before proceeding with the titration of a chloride with silver nitrate.

W. P. S.

**Gravimetric Analysis. XIII. Estimation of Sulphuric Acid. III.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1920, **33**, 159—160, 162—163. Compare this vol., ii, 329).—Tables are given showing the corrections to be applied to the weight of barium sulphate precipitates for the effect of alkali chlorides and other salts on the precipitation. The presence of ammonium chloride decreases the effect of other salts.

A summary is given of conditions of precipitation, and of corrections to be applied, as detailed in the earlier parts, in order to obtain trustworthy results. W. P. S.

**Estimation of Nitro-groups by a Modification of Young and Swain's Method.** LOUIS DESVERGNES (*Ann. Chim. anal.*, 1920, [ii], **2**, 141—143).—Many nitro substances, when dissolved in sodium hydroxide solution, yield a brown coloration, which interferes with the iodometric estimation of the excess of stannous chloride used in Young and Swain's reduction method (*A.*, 1898, ii, 186); it is therefore recommended that alcohol be used for dissolving the substance. The alcoholic solution is heated for two hours with an excess of stannous chloride solution in an atmosphere of carbon dioxide, and the excess is titrated subsequently with iodine solution. The method is trustworthy with a large number of nitro-substances, but not so in the case of nitrophenols and nitronaphthalenes. W. P. S.

**Apparatus for the Estimation of Nitric Nitrogen by Devada's Method.** JOSEPH ERLICH (*Ann. Chim. anal.*, 1920, [ii], **2**, 143—153).—The apparatus consists of a flask in which the nitrate is reduced by means of Devada's alloy, a condenser, and a receiver. The flask is connected with the condenser by a bulbous tube containing glass balls to prevent spray passing over into the receiver; a tube extends down the centre of this bulbous tube, and is used for passing a current of air through the apparatus towards the end of the operation. W. P. S.

**Colour Changes of the Diphenylamine Reaction.** E. M. HARVEY (*J. Amer. Chem. Soc.*, 1920, **42**, 1245—1247).—A modified diphenylamine reagent for use in microchemical tests for nitrates consists of 0.05 gram of diphenylamine, 7.5 c.c. of sulphuric acid (95—96%), 2.5 c.c. of 10% aqueous potassium chloride solution; or, if it is particularly desirable to avoid darkening of tissue, 5 c.c. of sulphuric acid, 3 c.c. of glacial acetic acid, and 2 c.c. of 12% aqueous potassium chloride solution may be used, at some sacrifice of colour intensity. A diagram shows that over the ranges 0—41%, 41—46%, 46—83%, 83—87%, 87—100%, with maxima of intensity at 38%, 71%, and 100% of sulphuric acid, the colours observed are oriental green to yellow, bluish-green, blue, colourless, and purple, respectively. The proportion of diphenylamine is variable between fairly wide limits, but in excess it interferes with the reaction; variations of temperature between 20° and 50°

have little effect; potassium chloride causes not only an intensification of the blue colour, but an extension in both directions of the concentrations of sulphuric acid which produce it, and it is more suitable for this purpose than sodium chloride, owing to the greater solubility of its acid sulphate. The stability of the blue colour once produced, even in concentrations of acid in which normally it would not be produced, renders the order of mixing of some importance. J. K.

**Denigès's Strychnine-Molybdate Reaction.** L. DÉBOURDEAUX (*Bull. sci. pharmacol.*, 1920, 27, 70—72).—In order to detect phosphates in the presence of barium, the preparation of Denigès' strychnine-molybdate reagent has been modified as follows: Strychnine (1.17 grams) is dissolved on a boiling water-bath in 200 c.c. of water and 8 c.c. of nitric acid (1:9). Ammonium molybdate (75 grams) is dissolved in 50 c.c. of water, the solution is mixed while cold with 50 c.c. of nitric acid (D 1.20), digested at 40° for four days, and the clear solution decanted or filtered through glasswool. Thirty c.c. of this solution and 30 c.c. of nitric acid (1:9) are added to the strychnine nitrate solution, and the whole is made up to 300 c.c. The reagent thus prepared is at first colourless, but acquires finally the colour of picric acid, at which point it has reached its maximal sensitiveness. This occurs about the eighth or tenth day, although the reagent can be used on the third day. The sensitiveness persists for two to three months, but only 1% remains after five to six months. The sensitiveness depends largely on the molybdate solution, which must be freshly prepared as described. CHEMICAL ABSTRACTS.

**Estimation of Small Amounts of Phosphoric Acid as Barium Phosphomolybdate in the Presence and in the Absence of Phosphorus in Organic Combination.** S. POSTERNAK (*Bull. Soc. chim.*, 1920, [iv], 27, 507—518).—It is possible to estimate amounts of phosphorus as small as 0.05 mg. by precipitation and weighing as barium phosphomolybdate from the corresponding ammonium salt in a medium containing, in addition, only sulphate alone or nitrate alone.

In the absence of organic matter, the inorganic phosphorus is precipitated from hot solution in the presence of 5% of sulphuric acid and 10% of ammonium sulphate. The ammonium phosphomolybdate precipitate is washed four times with a 5% solution of ammonium nitrate, then dissolved in a little ammonia, and reprecipitated with a 10% solution of barium chloride. The precipitate is collected, washed with water, dried, and calcined at a red heat. It has the constitution  $4\text{Ba}_2[\text{PO}_4(\text{MoO}_4)_2]_2 \cdot \text{Ba}_2[\text{SO}_4(\text{MoO}_4)_2]$ , and its weight when multiplied by 0.00739 gives the weight of phosphorus present.

In the presence of organic compounds of phosphorus, the inorganic phosphorus is first precipitated at 15° in a medium containing at least 5% of ammonium nitrate. The precipitate of

barium phosphomolybdate finally obtained in this case has the constitution  $8\text{Ba}_{27}[\text{PO}_4(\text{MoO}_4)_{12}]_2\cdot\text{Ba}_1(\text{MoO}_4)_4$ , and the factor for converting its weight into weight of phosphorus is 0.00786. Under these conditions, none of the organic phosphorus is precipitated.

W. G.

**Presence of Phosphates in Human Blood. X. The Nephelometry of Phosphoric Acid in Analyses which deal with Quantities of the Order of Magnitude employed in Bang's Method as a Means of Studying the Distribution of Phosphorus, especially in Lecithinæmia.** JOH. FEIGL (*Biochem. Zeitsch.*, 1920, 102, 131—141).—A detailed discussion of the technique of the above method.

S. S. Z.

**Some Quick Methods for [the Detection of] Arsenic and Antimony.** CHAS. W. CUNO (*Proc. S. Dakota Acad. Sci.*, 1919, 3, 34—47).—The following methods are sensitive to 0.1%. (1) The substances in acid solution are precipitated by hydrogen sulphide, the precipitate is well washed and extracted several times with an ammoniacal solution of ammonium carbonate to remove arsenio sulphide, which is then reprecipitated by concentrated hydrochloric acid; copper interferes very little if the precipitate has been well washed. Antimony sulphide is removed from the precipitate by repeated washing with a hot solution of sodium carbonate; by using small quantities and re-heating each time, the antimony is obtained in concentrated solution, and separates, on cooling, almost quantitatively at 0°. Tin is removed from the sulphide precipitate by sodium hydroxide solution, and is detected in the usual way.

(2) When copper and mercury are not present, a solution of the ore in hydrochloric acid is treated with sodium thiosulphate, whereby arsenic, antimony, and bismuth are precipitated, but not cadmium and tin. The precipitate is boiled with concentrated hydrochloric acid, when the arsenic remains undissolved. When arsenic, antimony, tin, copper, cadmium, and bismuth are all present the material is dissolved in hydrochloric acid, and the solution is warmed with a concentrated solution of sodium thiosulphate, whereby arsenic only is precipitated, together with some sulphur; by diluting the solution to six volumes and warming, antimony will first appear as a red coloration, which is quickly masked by the other metals.

(3) When copper is absent, arsenic can be detected by dissolving the substance in concentrated hydrochloric acid and passing a rapid stream of hydrogen sulphide into the concentrated solution; no other metal except copper is precipitated in concentrated hydrochloric acid solution.

CHEMICAL ABSTRACTS.

**Estimation of Small Quantities of Arsenic.** K. SCHERINGA (*Pharm. Weekblad*, 1920, 57, 420—421).—A slight modification in the Bloemendal arsenic apparatus is described. The estimation

of arsenic in urine is carried out as follows: 500 c.c. of urine are evaporated to dryness with 30 grams of pure sodium chloride. The residue is transferred to a distillation flask, and 30 c.c. of pure concentrated sulphuric acid are added. As much as possible of the hydrogen chloride is distilled over and is absorbed in 100 c.c. of saturated sodium carbonate solution. To the solution, a slight excess of bromine is added, and then 5 c.c. of 10% sodium phosphate solution and 5 c.c. of ammoniacal magnesia mixture. The precipitate is dissolved in dilute sulphuric acid, reduced, and the solution transferred to the apparatus. This procedure is applicable to most organic substances containing arsenic. W. S. M.

**Rapid Estimation of Arsenic in Commercial Sulphuric Acid.** A. A. Kohn (J. Ind. Eng. Chem., 1920, 12, 580—581).—

For the estimation of arsenious arsenic, 20 grams of acid are diluted with water, and a few drops of methyl-orange added. The solution is neutralised with sodium carbonate solution until it is very faintly pink, and about 2 grams of powdered sodium hydrogen carbonate are then added. The solution, after dilution with water to 250 c.c., is titrated with 0.1N-iodine and starch, a blank test being made. For determining the arsenic in the arsenic form, 20 grams of acid are heated for one hour in an oven at 105—110°. It is then diluted with a little water, and a saturated solution of sodium hydrogen carbonate added in slight excess, phenolphthalein being used as indicator. The solution is boiled and filtered. Three grams of powdered sodium hydrogen carbonate are added, and 150 c.c. of hydrochloric acid slowly poured in with agitation, after which 1 gram of potassium iodide is added, and air excluded. After agitation and remaining for five minutes, the solution is titrated with 0.1N-thiosulphate and starch. The reaction,  $\text{H}_3\text{AsO}_3 + \text{I}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{AsO}_4 + 2\text{HI}$ , proceeds from left to right when the concentration of the hydrogen ion is low; and there should be few OH ions. In presence of sufficient hydrogen chloride, the reaction goes from right to left. Copper salts interfere in the arsenic determination but are usually negligible. If in appreciable amount, they must be estimated, and a correction applied to the thiosulphate titration. W. J. W.

**The Acidimetric Estimation of Boric Acid.** J. A. M. VAN LIEMPT (Zeitsch. anorg. Chem., 1920, 111, 151—166).—See this vol., ii, 331.

**Estimation of Carbon Dioxide in Moorland Waters.** V. ROHR (Chem. Zeit., 1920, 44, 469).—In titrating the free carbon dioxide and that present as hydrogen carbonates in moorland waters, errors are caused by the presence of weak organic acids and their salts, which are simultaneously titrated. Winkler's method (Zeitsch. Nahr. Genussm., 1910, 20, 617) of removing free carbon dioxide by repeatedly spraying the water would scarcely be applicable on a small scale. When the solvent action of moorland



water on limestone is to be determined, Heyer's method (*Gesundheitsing.*, 1912, **35**, 669) may be employed. The water is shaken at frequent intervals with powdered marble in a closed flask, and a portion then titrated with *N*/10-acid (methyl-orange as indicator). The difference between the result and that obtained by titrating the water, without treatment with marble, gives the amount of calcium carbonate dissolved by the water. C. A. M.

**Use of the Jamin Interferometer for the Estimation of Small Amounts of Helium or Hydrogen in Air.** J. C. McLENNAN and R. T. ELWORTHY (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 19—25).—A method for the estimation of small amounts of helium and hydrogen in air by means of the Jamin interferometer is described. Two methods of calibrating the instrument are outlined, one based on the relation between the difference in path caused by the displacement of air in one tube by the mixture and the resulting shift of bands, and the second based on the change of refractive index of the air in one tube caused by lowering the pressure of the air. The accuracy was  $\pm 0.5$  per cent. With longer tubes, a greater accuracy could be obtained.

J. R. P.

**Estimation of the Helium Content of Mixtures of Gases by the Use of a Katharometer.** V. F. MURRAY (*Trans. Roy. Soc. Canada*, 1919, **13**, iii, 27—35).—The Shakespear Hydrogen Purity Meter, high and low percentage explorers, and a Shakespear Permeameter Explorer have been calibrated for use with helium.

J. R. P.

**Application of a New Physico-chemical Method of Analysis to the Study of Double Salts.** RENÉ DUBRISAY (*Compt. rend.*, 1920, **170**, 1582—1584).—The method employed is based on the observation of the temperature of mixing the solutions with an invariable liquid (compare A., 1919, i, 73; ii, 78), phenol being used. If a mixture of solutions of sodium sulphate and potassium sulphate is thus mixed with phenol, the temperature of mixing observed agrees closely with that calculated from the law of additivity. If, however, a mixture of solutions of potassium sulphate and zinc sulphate is used, there is a variable difference between the observed and calculated results, the maximum variation corresponding with equimolecular proportions of the two salts, and indicating the presence, in solution, of a double salt. W. G.

**Estimation of Alkali as Sulphate with Special Reference to the Alkali Salts of Organic Acids.** C. F. VAN DEN (*Chem. Weekblad*, 1920, **17**, 283—284).—The usual procedure is modified as follows: The alkali salt is evaporated with concentrated sulphuric acid until fuming ceases. The residue of sulphate and pyrosulphate is dissolved in ammonium carbonate solution. The solution is evaporated to dryness on asbestos and the residue gently ignited. In this way, no losses by spitting are incurred, and any carbonaceous matter is easily burned off. W. S. M.

**Sensitiveness and Applicability of Qualitative Reactions.**

**I. Potassium Ions.** O. LUTZ (*Zeitsch. anal. Chem.*, 1920, **59**, 145—165).—The sensitiveness of various reactions for potassium was determined, the different tests being made as far as possible under the same conditions. In each test, 5 c.c. of potassium chloride solution were treated with the reagent, the temperature was kept at 18°, and the observation made after five minutes' contact; the following are the minimum concentrations of potassium which gave a reaction with the reagents: perchloric acid, 1:435; phosphomolybdic acid, 1:561; platinum chloride, 1:587; sodium borofluoride, 1:970; aniline hydrosilicofluoride, 1:1022; sodium phosphotungstate, 1:2170; phosphotungstic acid, 1:2809; sodium cobaltinitrite, 1:25,000; sodium-bismuth thiosulphate, 1:57,000; sodium picrate, 1:840; sodium 1-amino- $\beta$ -naphthol-6-sulphonate, 1:1022; sodium hydrogen tartrate, 1:1050. It is suggested that the results might also be expressed in actual quantities of potassium; for instance, the concentration 1:435 (perchloric acid test) would be  $11 \times 10^{-3}$  grams of potassium per 5 c.c. W. P. S.

**Analysis of Ingredients for Pyrotechnics.** HENRY B. FABER and WILLIAM B. STODDARD (*J. Ind. Eng. Chem.*, 1920, **12**, 576—578).—Sodium nitrate occurring in potassium nitrate in quantities as low as 0.01% may be estimated by a modification of Ball's method (T., 1909, **95**, 2126; 1910, **96**, 1408).

Instead of a separating funnel, a series of 30 c.c. Erlenmeyer flasks may be used for the precipitation of the caesium sodium bismuth nitrite. One gram of potassium nitrate is dissolved in 5 c.c. of water, 1 c.c. of 2*N*-nitric acid added, and 10 c.c. of the reagent. The flasks are connected, and the air is displaced by coal gas, one end of the series then being closed by a plug and the other by a Bunsen valve. After remaining for forty-eight hours in a cool place, the precipitate is collected on a Gooch crucible and washed with dilute, and then pure, acetone, the process being carried out rapidly to minimise exposure to air. The crucible is finally dried in an air-bath at 100° for thirty minutes, and the weight of sodium calculated from the weight of precipitate  $\times 0.03676$ . Alternatively, the precipitate may be treated with 150 c.c. of water, 0.1*N*-potassium permanganate added in excess, and 40 c.c. of sulphuric acid (1:1), the solution being heated to 70° and titrated with 0.1*N*-sodium oxalate. The available oxygen of the permanganate consumed  $\times 7.820$  gives the weight of caesium sodium bismuth nitrite.

For the determination of nitrates, 1 gram is mixed with 5 grams of tungsten trioxide in a platinum crucible and heated over a Bunsen for ten minutes. The loss in weight represents oxygen and oxides of nitrogen, and enables the percentage of pure nitrate to be calculated.

For estimating aluminium in flakes or powders, its reducing power on lead oxide is utilised. Three grams of aluminium are mixed with 100 grams of litharge and 30 grams of borax glass in

a fireclay crucible, a covering layer of 25 grams of borax glass being added. The mass is fused in a muffle for twenty minutes. The lead is then separated from the slag and weighed, the factor 0.0872 giving the equivalent aluminium. A high temperature should be employed to reduce the time of fusion and minimise re-oxidation of the lead.

W. J. W.

**A Method for the Determination of the Ion Concentration in Ultra Filtrates and other Protein-free Solutions.** R. BRINKMAN and (Miss) E. VAN DAM (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 762—771).—A simple method for measuring the concentration of calcium ions in a solution of a mixture of salts is based on the following principle. To a solution containing  $\text{Ca}^{++}$ , there are added oxalate ions until the solubility of calcium oxalate is just reached. A slight milkiness appears directly this point is passed. The method is correct to 2—3 mg. of calcium per litre. The principle of the method can be applied to the estimation of other ions. The only condition is the employment of a reagent that will give a very sparingly soluble salt with the ion the concentration of which is to be measured.

J. C. D.

**Colorimetric Method for the Estimation of the Copper and Iron Present in Lead and Lead Oxides.** CHARLES R. HARDY (*Chem. News*, 1920, 120, 256).—A rapid method of estimating small quantities of iron and copper in metallic lead or litharge. The sample (200 grams) is dissolved in nitric acid (D 1.2) and diluted as the action proceeds to prevent lead nitrate crystallising. The solution is treated with concentrated sulphuric acid (32 c.c. per 100 grams of sample) and the precipitate allowed to settle. The solution is decanted four or five times, treated with 10 c.c. of sulphuric acid, and evaporated nearly to dryness. After cooling, the liquid is diluted with water and filtered. The filtrate is evaporated to small bulk, treated with a few drops of nitric acid, boiled and treated with ammonia. The precipitate is filtered, redissolved, and reprecipitated. The filtrates from the iron contain all the copper; these are evaporated and the volume made up to 50 c.c. The measured quantity is made ammoniacal and boiled until quite neutral. When cold, the solution is placed in a Nessler glass, 5 c.c. of potassium ferrocyanide solution (0.4%), and 5 c.c. of ammonium nitrate solution (10%) added. In a second Nessler glass, 5 c.c. of ferrocyanide and 5 c.c. of ammonium nitrate are placed, and the volume made the same as that in the first glass with distilled water. A standard solution of copper (0.393 gram  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  per litre) is added from a burette until the colour in both glasses is the same.

The iron precipitate is dissolved in a small quantity of nitric acid and made up to 250 c.c.; 25 c.c. is placed in a Nessler glass with 9 c.c. of 25% hydrochloric acid and 5 c.c. of ammonium thiocyanate solution (5%). In a second glass, 10 c.c. of 25% hydrochloric acid and 5 c.c. of thiocyanate solution are placed, and the volume made up to that in the first glass. A standard iron solu-

tion (0.210 grams ferrous ammonium sulphate per litre) is then run in from a burette until the tints of both are alike.

If red lead has to be examined, a 20-gram sample should be taken, dissolved in aqua regia, and sufficient water added to dissolve all the lead chloride.

J. F. S.

**Assay of Alunite.** EDWARD S. SIMPSON (*Chem. Eng. Min. Rev. Australia*, 1919, 11, 297—298).—The estimation of the total alunite is based on the fact that alunite is the only sulphate in the ore which is insoluble in water, but soluble in dilute sodium hydroxide solution; not uncommonly, a little calcium and magnesium sulphates are present, for which a correction must be made. Sulphates soluble in water are estimated by treating 0.7 to 0.8 gram of the ore with 100 c.c. of water, and after one hour estimating the dissolved sulphates as barium sulphate. Total sulphates are estimated by heating 0.7 to 0.8 gram of the ore with 60 c.c. of 5% sodium hydroxide solution on the steam-bath for one hour, with occasional stirring, and estimating the sulphate in the filtrate as barium sulphate. From the total sulphate are subtracted the sulphate found in a blank experiment and the water-soluble sulphate; the difference, expressed as a percentage of the ore and multiplied by 2.55, gives the percentage of alunite (including natro-alunite). The error may be +2%.

The estimation of the extractable alkali oxides in the ore is performed by heating 0.5 to 0.6 gram of the ore in a muffle furnace at 819° during one hour (freshly fused sodium chloride is used to indicate the temperature; the temperature must not exceed 877° [m. p. of lead oxide]), and, after cooling and weighing, extracting the residue with boiling water and treating the filtrate with 7 c.c. of barium chloride solution (122 grams in a litre) and 0.6 gram of hydrated barium hydroxide; after removing the excess of barium and the calcium in the usual way, the total alkali chlorides and the potassium chloride (as platinichloride) are estimated by the usual methods. The results, corrected by the amounts found in a blank experiment, are expressed as percentages of the raw ore and of the roasted ore. CHEMICAL ABSTRACTS.

**Rapid Volumetric Method for the Estimation of Iron, Applicable in the Presence of Hydrochloric Acid, Phosphorus, Oxy-acids, and Organic Matter.** H. DROOP RICHMOND and EDITH M. ISOX (*Analyst*, 1920, 45, 258—260).—The following method gives trustworthy results for the estimation of iron in many pharmaceutical preparations. From 5 to 10 c.c. of the sample are treated with a few drops of hydrochloric acid, and N/10-permanganate solution is added until a transitory purple coloration is produced throughout the solution. An equal volume of concentrated hydrochloric acid is then added, followed by a small quantity of sodium hydrogen carbonate (to give an atmosphere of carbon dioxide), and N/10-stannous chloride solution is run in drop by drop until a drop of the mixture gives a blue

coloration with potassium ferrieyanide solution. The mixture is then titrated with  $N/10$ -stannous chloride solution, using thio-cyanate solution as an external indicator. The number of c.c. of  $N/10$ -stannous chloride solution used in the titration is multiplied by 0.0056 to obtain the quantity of iron present. W. P. S.

**Estimation of Iron and Separation of Manganese from Iron by the Ammonium Salt of Nitrosophenylhydroxylamine (Cupferron).** E. H. ARCHIBALD and RUTH V. FULTON (*Trans. Roy. Soc. Canada*, 1919, 13, iii, 243—253).—The cupferron precipitate of iron is slightly soluble in the acid solution from which it is precipitated. The solubility is apparently not affected by the substitution of sulphuric for hydrochloric acid, but is appreciably lowered by adding ammonium chloride to the solution. The precipitate is slightly soluble in the wash-water. If corrections are applied for these solubilities, the method is very exact. Iron can be separated from manganese in a solution containing four times as much manganese as iron, the amount of manganese carried down by the precipitate being inappreciable for most purposes. The amount increases with the acid dilution of the mother liquor. The presence of ammonium chloride to the extent of 5 grams in 100 c.c. of solution is an advantage in the separation. J. R. P.

**Use of the Rotating Zinc Reductor in the Estimation of Molybdenum.** WALTER SCOTT (*J. Ind. Eng. Chem.*, 1920, 12, 578—580).—The rate of reduction of molybdic acid by zinc is nearly as rapid between 26° and 30° as at the boiling point. Reduction is not appreciably affected by the aid of an electric current. By covering the beaker with a split cover-glass during the operation, enough hydrogen is retained to act as a protective covering for the zinc. The reduced solution may be titrated with permanganate in the same beaker; if it is transferred to another vessel, it must be poured into ferric alum and syrupy phosphoric acid. W. J. W.

**Bibliography of the Analysis of Antimony.** ELTON R. DARLING (*Chem. Eng.*, 1919, 27, 11, 12, 63; from *Chem. Zentr.*, 1919, ii, S99; 1920, ii, 750).—A compilation of English, French, and German literature on the subject. E. H. R.

**Process for Testing Air for the Presence of Combustible Substances.** E. BECKMANN [with KURT SEGLICH] (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, 34, 924—936).—Two pieces of apparatus have been designed, primarily to test the air of coal mines in respect of explosibility due to the presence of methane. That for the preliminary test consists of a cylinder fitted with a piston and inlet valve for collection of the sample, which is exploded by means of pyrophoric iron, the heat generated causing a temporary expansion, which is registered by a manometer. A locking device ensures that the igniter shall not be operated until

the inlet valve is closed. Explosion only takes place when 7—10.3% of methane is present, but the limits can be widened somewhat by compression of the gas and by use of a catalyst, although its untrustworthiness renders the latter not very suitable for practical purposes. Addition of methane or air with the same object to samples outside the limits given is also liable in practice to lead to erroneous results. The second apparatus is a metal cylinder, containing potassium hydroxide, connected to a suction pump which serves to fill the vessel with air to be tested, and to a mercury manometer which indicates the contraction due to absorption of the carbon dioxide and water resulting from combustion of the methane. Ignition is secured by a platinum spiral, made white-hot by a current for the space of two minutes, the time being regulated by a mercury contact on the principle of the ordinary sand-glass. A non-return valve protects the manometer from the initial force of explosion, and provision is made for the automatic sounding of an electric alarm to follow a contraction due to a proportion of methane in excess of the safety limit. A determination takes about three minutes, and a form of the apparatus has been developed by which analyses are automatically made and registered every half-hour. As the gas examined is not filtered, any dust present exerts the same effect as it would do in an actual explosion. The explosions diminish in intensity with increase in the proportion of methane, and no longer occur when this reaches 16%. Further, in consequence of the increasing formation of carbon monoxide and hydrogen in these circumstances, the degree of contraction observed gradually diminishes and gives place to an expansion when 20% or more of methane is present. Any uncertainty as to the meaning of a small contraction is removed by repetition of the determination after admixture of air with the gas under examination. Hydrogen and illuminating gas may be detected by the first apparatus between limits of 9 and 42%, 8 and 25% respectively; further, the fact that a red heat suffices to initiate their combustion in the second apparatus supplies a means of detecting these gases in presence of methane. J. K.

**Estimation of Acetylene in Coal Gas and Air by Means of Ilosvay's Reagent.** H. ARNOLD, E. MÖLLNEY, and F. ZIMMERMANN (*Ber.*, 1920, **53**, [B], 1034—1039. Compare Ilosvay de Nagy Ilosva, A., 1900, ii, 52).—The coal gas is shaken in a separating funnel of about 3 litres capacity with about 20 c.c. of the reagent at intervals during an hour; the precipitate is filtered and well washed with water containing hydroxylamine. The precipitate and filter are treated in a crucible with a little concentrated nitric acid, the solution is evaporated, and the residue ignited and weighed as copper oxide. The results obtained in this manner are sometimes high, due to the presence of impurities derived from the reagents in the precipitated copper acetylide, but this drawback may be overcome by dissolving the precipitate from the filter with nitric acid and evaporation of the filtrate.

Test analyses with mixtures of acetylene and air show the method

to be very accurate, and to be available even when not more than 0.04% of acetylene is present; at such dilutions, however, it is necessary to add about 5% of carbon dioxide to the mixture, since otherwise the results are low as a consequence of atmospheric oxidation. The process can also be used for the estimation of acetylene in coal gas, from which hydrogen sulphide, if present, must be removed; this can be effected by dry copper sulphate-pumice.

H. W.

**Volumetric Estimation of Acetylene.** RICHARD WILLSTÄTTER and ERNST MASCHMANN (*Ber.*, 1920, 53, [B], 939—941).—Methods of estimating acetylene, which are based on its reaction with silver nitrate and titration of the nitric acid liberated in accordance with the equation  $C_2H_2 + 3AgNO_3 = C_2Ag_2 + AgNO_3 + 2HNO_3$ , are found to be untrustworthy, since it has not been found possible to find conditions under which a molecule of the gas liberates two molecules of nitric acid, the amounts of acid actually set free varying from about 0.5 mol. in alcoholic, to about 1 mol. in aqueous solution. The following procedure gives trustworthy results. Acetylene, in gaseous form or in solution, is agitated for a few minutes with Hoesvay's reagent freshly prepared from copper nitrate, ammonia, and hydroxylamine hydrochloride, and the precipitated copper acetylide is filtered through an asbestos filter and washed until the filtrate no longer decolourises *N*/10-permanganate, care being taken not to allow the precipitate to become dry. The copper acetylide is washed from the asbestos by means of about 25 c.c. of a solution prepared by making up ferric sulphate (100 grams) and concentrated sulphuric acid (200 grams) to a litre with water. The ferrous sulphate, formed in accordance with the equation  $C_2Cu_2 + Fe_2(SO_4)_3 + H_2SO_4 = FeSO_4 + 2CuSO_4 + C_2H_2$ , is estimated by titration with *N*/10-permanganate. The liberated acetylene does not introduce any complication. Test analyses with pure and diluted acetylene show the method to be accurate.

H. W.

**Estimation of Chloroform and other Volatile Substances.** A. SCHLICHT and WALTER AUSTEN (*Zeitsch. öffentl. Chem.*, 1920, 26, 55—57).—To estimate chloroform in admixture with alcohol, 5 c.c. of the mixture are diluted with water to 200 c.c. and shaken with 60 c.c. of ether; after the ethereal layer has separated, its specific gravity is determined. An increase of 0.0001 in the specific gravity corresponds with 0.1786 gram of chloroform in 100 c.c. of the original mixture.

W. P. S.

**Thermal Analysis of the Products of Nitration of Naphthalene.** P. PASCAL (*Bull. Soc. chim.*, 1920, [iv], 27, 388—408).—A study of the melting point curves of the binary mixtures, naphthalene- $\alpha$ -nitronaphthalene; 1:5-dinitronaphthalene-1:8-dinitronaphthalene;  $\alpha$ -nitronaphthalene-1:5-dinitronaphthalene;  $\alpha$ -nitronaphthalene-1:8-dinitronaphthalene; 1:5-dinitro-

naphthalene-1:3:5-trinitronaphthalene; 1:8-dinitronaphthalene-1:3:5-trinitronaphthalene; 1:5-dinitronaphthalene-1:3:8-trinitronaphthalene; 1:8-dinitronaphthalene-1:3:8-trinitronaphthalene; 1:3:8- and 1:2:5-trinitronaphthalenes; 1:3:5- and 1:2:5-trinitronaphthalenes; 1:3:5- and 1:3:8-trinitronaphthalenes; 1:4:5- and 1:3:8-trinitronaphthalenes; 1:4:5- and 1:2:5-trinitronaphthalenes; and of the ternary mixtures, nitronaphthalene and the two dinitronaphthalenes; the two dinitronaphthalenes and each of the trinitronaphthalenes in turn; 1:3:5-, 1:3:8-, and 1:2:5-trinitronaphthalenes. The application of these results to the analysis of industrial products of nitration of naphthalene is discussed.

W. G.

**Estimation of Methyl Alcohol.** A. HEIDUSCHKA and L. WOLF (*Pharm. Zentr.-h.*, 1920, **61**, 361—366).—The methyl alcohol is heated at 100° for an hour in a closed vessel with sulphuric acid and an excess of potassium dichromate; the quantity of carbon dioxide formed is then estimated gravimetrically by absorption in potassium hydroxide solution. The excess of dichromate is estimated volumetrically, and the quantity of methyl alcohol present is calculated from the weight of carbon dioxide formed or from the amount of oxygen required for the oxidation. The method may be applied to a mixture of methyl and ethyl alcohols, an allowance being made for the fact that 0.8% of the ethyl alcohol is also oxidised to carbon dioxide. [See, further, *J. Soc. Chem. Ind.*, 1920, 558A.] W. P. S.

**Estimation of Ethylene Glycol.** BERNHARD MÜLLER (*Chem. Zeit.*, 1920, **44**, 513—515).—Ethylene glycol, now used as substitute for glycerol in Germany, may be estimated by the dichromate or acetic methods used in glycerol analysis, but the acetic method cannot be used for dilute solutions of the glycol. Oxidation with chromic acid and sulphuric acid, and gravimetric estimation of the carbon dioxide produced, also yields trustworthy results. Ethylene glycol does not appear to be oxidised completely to oxalic acid by permanganate in alkaline solution. W. P. S.

**Analysis of Powders and Explosives. Differentiation of Glyceryl Trinitrate and of Ethylene Dinitrate.** M. D. MARQUEYROL and E. GOUTAL (*Bull. Soc. chim.*, 1920, [iv], **27**, 443—448).—When exposed in a desiccator over sulphuric acid at 12° and at the ordinary pressure, glyceryl trinitrate does not lose in weight, whereas ethylene dinitrate loses steadily. When a mixture of the two is so exposed, the loss in weight is directly proportional to the percentage of the latter in the mixture.

In 10% solution, glyceryl trinitrate and ethylene dinitrate cause respectively a lowering of 2.13° and 3.06° in the freezing point of benzene. With mixtures, the lowering is proportional to the amounts of the two substances present.

Either of these methods may be used for estimating the amount



of ethylene dinitrate in a sample of glyceryl trinitrate, and neither is vitiated by the presence of commonly occurring impurities, such as vaselin, diphenylamine, etc.

W. G.

**Estimation of Glyceryl Nitrate.** H. DROOP RICHMOND (*Analyst*, 1920, **45**, 260—265).—A method for the analysis of commercial "nitroglycerin" solution consists in diluting 10 c.c. of the sample with 50 c.c. of water and titrating the acidity with  $N/10$ -barium hydroxide solution; 0.1 c.c. is deducted from the volume of the latter solution required, and the result is divided by 1.02. To estimate the glyceryl nitrate, 5 c.c. of a 10% solution plus 5 c.c. of 90% alcohol, or 10 c.c. of a 5% solution, are treated with 25 c.c. of  $N/2$  alcoholic sodium hydroxide solution; 20 c.c. of a 1% solution require 10 c.c. of the alkali solution. After five minutes, phenolphthalein is added, and the excess of alkali titrated with  $N/1$ -acid. If more than 4 c.c. of acid is used, the estimation must be repeated, increasing the quantity of alcohol, as the amount of water introduced must not exceed 10% of the total volume. The volume of alkali solution absorbed is corrected for the acidity; each c.c. of  $N/1$ -sodium hydroxide solution corresponds with 0.05675 gram of nitroglycerol. If 2 c.c. of 100 vol. hydrogen peroxide are added before the alkali is introduced, the final alcoholic strength has much less influence on the titration.

W. P. S.

**Volumetric Estimation of  $\beta\beta$ -Dichloroethyl Sulphide.** WILLIAM FRANCIS HOLLELY (*T.*, 1920, **117**, 898—902).

**The Analysis and Composition of "Cresylic Acid."** J. J. FOX and M. F. BARKER (*J. Soc. Chem. Ind.*, 1920, **39**, 169—172r).—The "cresylic acid" used consisted of the tar acids distilling up to  $210^{\circ}$  and then refractionated up to  $203^{\circ}$  or  $204^{\circ}$ , such a fraction usually containing less than 10% of phenol. If more phenol is present, its proportion should be brought below 10% by adding a suitable amount of *m*-cresol. It is shown that Raschig's nitration process (*A.*, 1900, ii, 691) for the estimation of *m*-cresol is sufficiently accurate for technical purposes. The authors obtained the best results by a slightly modified procedure in the first stage of the process. Ten grams of the "cresylic acid" are heated with 15 c.c. of 98% sulphuric acid in a 1200 c.c. flask until the liquid is viscous at the room temperature. By rotation, the liquid is spread in a thin layer over the bottom of the flask and 100 c.c. of nitric acid (D 1.4) is added, and the flask replaced on the water-bath. Raschig's procedure is then followed.

The following bromination method will give accurate results. One gram of the dried "cresylic acid" is weighed into a tared flask fitted with a ground-in stopper carrying a tap-funnel and an exit tube with a stopcock. Excess of a 20% solution of bromine in carbon tetrachloride is added drop by drop, and the mixture left for several hours. It is then warmed at a temperature not

exceeding 50° to expel bromine, and finally the solvent is distilled off under reduced pressure. The products of bromination are then weighed. The percentage of *m*-cresol is given by the equation  $\%m\text{-cresol} = (100W - 246.3)/0.731$ , where *W* is the weight of bromo-derivative obtained from 1 gram of the mixed cresols.

A modification of the method of Ditz and Cedivoda (A., 1900, ii, 54), in which the amount of bromine absorbed during bromination is estimated volumetrically, was found to be very rapid and sufficiently accurate for general work.

By estimating the percentage of *m*-cresol by one of these methods, and the percentage of phenol by the method previously described (A., 1917, ii, 513), or that of Dawson and Mountford (T., 1918, 113, 923), and determining the  $D_{540}^{1\%}$  of the mixture of cresols, the percentage of *o*-cresol present is given by  $0.0128O = 100(G - 1.0388) - 0.0386P$ , where *O* is the percentage of *o*-cresol, *P* that of phenol, and *G* the value of  $D_{540}^{1\%}$ . The percentage of *p*-cresol is then obtained by difference from 100.

Finally, the authors reply to the criticisms of Dawson and Mountford (*loc. cit*) of the curves given in their last paper (compare A., 1918, i, 427).  
W. G.

**Titration of Sugars.** N. SCHOORL (*Zeitsch. Nahr. Genussm.*, 1920, 39, 180—182).—In the method described by Rupp and Lehmann (A., 1909, ii, 442) and Schowalter (A., 1919, ii, 172), the prescribed quantities of solutions must be employed in order that the tables may indicate the correct amount of dextrose. When an aliquot portion of the copper solution is titrated, the result must be corrected to the total volume before reference is made to the tables.  
W. P. S.

**Detection of Oxalic Acid and Lactic Acid and Differentiation from Tartaric Acid.** KURT BRAUER (*Chem. Zeit.*, 1920, 44, 494).—When heated with a mixture of concentrated sulphuric acid and resorcinol, oxalic acid yields a brilliant violet coloration, whilst tartaric acid and lactic acid give red colorations. Tartaric acid gives a yellow, oxalic acid a green, and lactic acid a red coloration when heated with dilute sulphuric acid (1:1) and resorcinol. The colorations obtained are less characteristic when the resorcinol is replaced by phloroglucinol, catechol, or quinol.  
W. P. S.

**A Reaction of Benzoic Acid Based on its Diazotisation; Its Application to the Toxicological Detection of Atropine, Cocaine, and Stovaine.** MARCEL GUERRET (*Compt. rend.*, 1920, 171, 40—41).—The following procedure gives a ready means of detecting as little as 0.0001 gram of benzoic acid, or of substances such as cocaine or stovaine which contain a benzoyl group, or of atropine which on oxidation yields benzoic acid. The small amount of material is placed on a watch-glass, three or four drops of nitric acid (*D* 1.49) are added, and the mixture evaporated to dryness

on a water-bath. The residue is taken up with one drop of a 10% solution of stannous chloride, and after two or three minutes' warming, the nitrobenzoic acids are reduced. The liquid is allowed to cool, and two drops of a 1% solution of sodium nitrite are added, and finally, three drops of a 1% solution of  $\beta$ -naphthol in ammonia, when a bright orange-red precipitate is obtained if benzoic acid or one of the alkaloids mentioned above was originally present. The test may be confirmed by dissolving the azo-compound in 1 c.c. of concentrated sulphuric acid and pouring the solution into water, an orange-yellow colour resulting.

For toxicological work, the test may be applied to the extracts of organs prepared by Stas's method. W. G.

**Analysis of "Saccharin."** OSKAR BEYER (*Chem. Zeit.*, 1920, **44**, 437—438).—To estimate *o*-bezoisulphinide in commercial "saccharin," 1 gram of the sample is titrated with *N*/10-potassium hydroxide solution, using phenolphthalein as indicator; the percentage quantity ( $x$ ) is then calculated from the formula

$$x = 2.01329 \times c - 100/0.09845,$$

where  $c$  is the number of c.c. of *N*/10-solution used. The difference between the result and 100 gives the amount of *p*-sulphamino-benzoic acid present, provided other impurities are absent.

W. P. S.

**Estimation of Acetaldehyde in Paracetaldehyde.** F. VON BRÜCHHAUSEN (*Apoth. Zeit.*, 1919, **34**, 428—429).—A description of experiments in view to the adaptation of an iodometric method, similar to that employed by Romijn in the case of formaldehyde, for estimating acetaldehyde in paracetaldehyde, whereby only negative results were obtained. Richter's sulphite method is best suited to the problem in question. CHEMICAL ABSTRACTS.

**Estimation of Phytin in Plant Extracts.** AUGUST RIPPEL (*Biochem. Zeitsch.*, 1920, **103**, 163—172).—Phytin can be precipitated more or less quantitatively in the presence of inorganic phosphates by copper acetate in acetic acid solution. Favourable results can only be obtained with definite concentrations of copper acetate and acetic acid. An extract from barley yielded 63.3% of the phytin- $P_2O_5$  by precipitation with copper acetate in a 1% acetic acid. The same method accounted for 92.8% of the phytin in standard solutions of that substance. The phytin in an acetic acid extract from peas could not be precipitated by copper acetate at all. S. S. Z.

**A New Microchemical Reaction of Cystine Applicable to its Detection in Urinary Calculi.** G. DENIGÈS (*J. soc. pharm. Bordeaux*, 1920, **58**, 8—12).—After pointing out the disadvantages of the methods in use at present, the author describes the following modified Esbach method for the identification of cystine in urinary calculi. A small quantity (1 mg. or more) of

the powdered or finely shaved material is placed on a glass slide, moistened with a drop of concentrated hydrochloric acid (D at least 1.17 or 1.18) added at the outer edge by means of a pointed glass rod, and examined under the microscope without the use of a cover-glass. The groups of prismatic needles, which rapidly increase in number, are cystine hydrochloride, and can be distinguished even with low magnification. After a few minutes, a drop of water is stirred in. The crystals will be observed to dissolve. This is characteristic of cystine hydrochloride, and serves to distinguish it from uric acid, which is insoluble under these conditions. The solution is evaporated to dryness over a flame, the residue is cooled, covered with a slip, and a drop of water is added at the edge. The formation of hexagonal plates of cystine will be observed after a few seconds. Two photomicrographs are presented showing the crystalline forms described.

## CHEMICAL ABSTRACTS.

**Estimation of Urea by Means of the Carbon Dioxide Evolved by Urease.** S. PARTOS (*Biochem. Zeitsch.*, 1920, 103, 292—299).—An apparatus is described by means of which urea is estimated from the carbon dioxide evolved from it by urease. Estimations of urea in artificial preparations, as well as in urine, are described which show only an error of the order of about 1%.  
S. S. Z.

**Rapid Detection of Morphine in the Toxicological Analysis of Viscera.** LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, 6, 349—351).—By means of the following method morphine was detected in the viscera after ingestion by the subject of only 0.002 gram: 120 grams of viscera are mixed with magnesia to a compact paste, which is completely dehydrated on the water-bath. The powdered residue is boiled with acetone, and the filtered extract treated with 2—3 c.c. of water and a few drops of acetic acid. The liquid is again filtered and evaporated on the water-bath. The residue containing the morphine is purified by treatment with 5% acetic acid, filtration, and extraction with boiling chloroform after addition of excess of ammonia.  
W. R. S.

**Reduction Potentials of Mixtures of Indigotin and Indigo-white, and of Mixtures of Methylene-blue and Methylene-white.** W. MANSFIELD CLARK (*J. Washington Acad. Sci.*, 1920, 10, 255—270).—Measurements were made at 30° of the reduction potential of indigotinsulphonic acid and of methylene-blue solutions during titration with titanium trichloride over a considerable range of  $P_H$  values, from 1.55 to 8.58. To obtain the required values of the hydrogen-ion concentration, "buffer" salts were used, consisting either of citrate or mixtures of this with other salts. It was found that the sharpness of the end-point depended on the  $P_H$  value of the solution. This accounts, perhaps, for the empirical observation of Knecht and Hibbert, that a sharp end-point in the titration of many dyes with titanium trichloride

can only be obtained in presence of such substances as tartrates. In the case of indigotinsulphonic acid, the reduction potential varied from +0.2076 at  $P_H=1.55$  to -0.1609 at  $P_H=8.58$ , and with methylene-blue from +0.3811 to -0.05 over the same range.

E. H. R.

**Goiffon's Colorimetric Method for the Estimation of Stercobilin.** V. BORRIEN (*Compt. rend. Soc. Biol.*, 1920, 83, 211—212; from *Chem. Zentr.*, 1920, ii, 723).—In Goiffon's method (this vol., ii, 399) a portion of the hydrobilirubin is carried down by the precipitate and remains on the filter. The accurate estimation of the substance is only possible when it has been isolated in the chemically pure condition, which has not been effected up to the present. For clinical purposes, methods such as that of Triboulet, which permit a rapid approximate estimation of the dye, are sufficiently accurate.

H. W.

**Estimation of Albumin in Urine containing Pus.** LUIS ESPINOSA TAMAYO (*Bol. Lab. Mun. Guayaquil*, 1920, 1, 33).—One hundred c.c. of filtered urine are treated with 1 c.c. of strong ammonia, stirred, and left to settle for a short time; in the presence of pus a gelatinous precipitate is formed, which is filtered off. The filtrate is treated with 20 c.c. of sodium chloride solution and 30% trichloroacetic acid to acid reaction; after half an hour's heating on the water-bath the precipitate is collected on a tared filter, and the determination completed as in Scherer's method. The albumin is easily filtered off.

W. R. S.

**Van Deen's Reaction and Hydrocyanic Acid.** LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1918, 6, 508—512).—Experimental proof is given that hydrocyanic acid, contrary to Selmi's statement (*Accad. Sci. Bologna*, 1879), does not interfere with Van Deen's reaction; on the other hand, potassium cyanide prevents the production of the blue coloration given by the reagent (hydrogen peroxide and tincture of guaiacum resin) in presence of fresh blood. This is shown to be due to the alkalinity of ordinary cyanide, as a positive reaction is obtained after neutralisation of the free alkali with acetic acid. Selmi's negative results must be attributed to the alkalinity of the cyanide used.

W. R. S.

**The Carbon Dioxide Content as a Basis for Distinguishing Heated from Unheated Milk.** LUCIUS L. VAN SLYKE and RICHARD F. KEELE (*J. Biol. Chem.*, 1920, 42, 41—45).—It appears that normal unheated milk seldom, if ever, has a vol. % of carbon dioxide lower than 3.5—3. Pasteurisation reduces this value to 2.5 or less. Therefore, it appears safe, in general, to assume that milk containing less than 2.5 or 3 vol. % of carbon dioxide has been heated to the temperature of pasteurisation.

J. C. D.

